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ANHYDROUS METANIOBATES AND METATANTALATES OF THE ALKALI METALS

I. METANIOBATES OF THE ALKALI METALS

M. A. Pchelkina and A. V. Lapitsky

The literature contains information about the preparation of lithium metaniobate [1], sodium metaniobate [2], and potassium metaniobate [3]. There are no data for the preparation of rubidium and cesium metaniobates.

Our objective was the preparation of rubidium and cesium metaniobates and a study of some properties of the metaniobates of the alkali metals.

EXPERIMENTAL

Starting Substances

Niobium pentoxide. The starting raw material for preparation of pure niobium pentoxide was the technical mixture known as "tantalum-niobium residue" containing the two elements in approximately 1:1 ratio. The principle extraneous substances present were oxides of iron, tin and silicon. The titanium content was negligible. For the preparation of pure niobium pentoxide, a certain amount of "residue" was mixed with 3 times its weight of 10% Na_2CO_3 and 90% NaOH and sintered at 700° in a silver dish. After cooling, the sintered mass was extracted from the beaker, pulverized in a porcelain mortar, transferred to a beaker and treated with distilled water. During the leaching process the tin and silicon went into solution in the form of sodium stannate and silicate, while the sodium niobate and tantalate (insoluble in presence of excess of alkali) remained in the residue. After two decantations the residue was dissolved in a large quantity of hot water to form a cloudy solution. The latter was filtered, and the filtrate was evaporated down before treating twice with 10% acetic acid solution; this treatment brought down a white, voluminous precipitate of the hydrated pentoxides of niobium and tantalum. For removal of the iron oxide, the precipitate was washed with acetic acid solution followed by 5% ammonium carbonate solution.

Separation of the niobium from the tantalum was effected by dissolving the mixture in 40% hydrofluoric acid. To the resultant colorless, transparent solution was added a saturated solution of potassium fluoride prepared in the amount required for formation of the double fluorides.

The acidity of the solution was about 2%, which is the optimum for complete separation of the two elements [4]. The crystals of potassium fluorotantalate were separated from the solution by filtration through a lead funnel, and they were washed with cold distilled water for removal of sodium oxyfluoroniobate solution. The wash liquors were combined with the filtrate which contained the main bulk of potassium oxyfluoroniobate ; the liquid was evaporated to dryness. The salt in the dish was heated to 120° and then dissolved in water by heating on a water bath. To the hot solution was added 0.5 ml hydrofluoric acid and 2 ml saturated potassium carbonate solution. A negligible amount of the salt, $K_4Ta_4O_5F_{14}$, came down after a short time and was filtered off. The above-described operation of tantalum separation was repeated but no precipitate was formed.

The solution of potassium oxyfluoroniobate was decomposed with concentrated ammonium hydroxide solution. The white precipitate of niobium pentoxide was washed first with dilute acetic acid solution and then with 5% ammonium carbonate solution.

Chemical analysis of the prepared niobium pentoxide, carried out by the known methods [5, 6, 7], showed that it was sufficiently pure and contained negligible amounts of impurities. A qualitative test for titanium [8] gave a negative result.

Spectrum analysis revealed an insignificant content of titanium, tantalum, iron and silicon. The lines of these elements were much less intense than the niobium lines.

Rubidium and cesium carbonates. We prepared these from chemically pure grades of the corresponding chlorides.

Weighed amounts of the starting salts were dissolved in the minimum amount of water. The resultant saturated solutions were treated with concentrated nitric acid while heating on a water bath. Excess of acid was taken. The end of the operation was indicated by the absence of chlorine in a check sample. The solutions of rubidium and cesium nitrates were treated with small portions of dry oxalic acid until oxides of nitrogen ceased to come off. The oxalates formed in this stage were heated in platinum dishes, gently at first and then strongly until completely converted into carbonates.

Preparation of Anhydrous Rubidium and Cesium Metaniobates.

Niobium pentoxide, previously calcined at 800° was thoroughly pulverized in an agate mortar and mixed with equimolar amounts of rubidium and cesium carbonates. The mixtures were transferred to platinum crucibles and heated at 800° for 4 hours. This period was required for completion of the reaction, as was indicated by the attainment of constant weight.

The prepared rubidium and cesium metaniobates were removed from their crucibles and treated with dilute hydrochloric acid for removal of any excess of the corresponding carbonate which had not reacted; the salts were then washed with water, dried, and calcined.

Both salts were analyzed for their content of niobium pentoxide and metallic oxide. A weighed amount of the salt was fused in porcelain crucibles with a tenfold amount of ammonium hydrosulfate. The transparent melts, after cooling, were treated with saturated ammonium carbonate solution. The contents of the beakers were heated on a water bath for an hour. The flocculent precipitates of niobium pentoxide were transferred to a filter and washed with 5% ammonium carbonate solution; after drying, the filters were ashed and the precipitates calcined to constant weight at 800°. The final weights gave the content of niobium pentoxide.

The filtrates contained, apart from rubidium (cesium) sulfate, considerable amounts of ammonium pyrosulfate and ammonium sulfate. The solutions were slowly evaporated to dryness on a water bath and then cautiously heated at a slightly higher termperature for removal of traces of water. After final dehydration, the sulfates were calcined; in this operation, as Spitsyn has shown [9], rubidium and cesium sulfates are fairly stable up to 800° whereas ammonium sulfate decomposes at a little above 350°. On attainment of constant weight, the rubidium and cesium were found in the form of sulfates.

Below are set forth the results of analyses of rubidium and cesium metaniobates.

Analysis of rubidium metaniobate.

Weights of samples 0.2008 and 0.2028 g.
Found %: Nb_2O_5 58.55, 58.86; Rb_2O 41.40, 41 32. $RbNbO_3$. Calculated %: Nb_2O_5 58.85; Rb_2O 41.15.

Analysis of cesium metaniobate.
Weights of samples 0.2018 and 0.2036 g.
Found %: Nb_2O_5 48.72, 48 34; Cs_2O 50.95, 50.82. $CsNbO_3$. Calculated %: Nb_2O_5 48.53; Cs 51.47.

The analytical data justify the conclusion that the prepared compounds are actually rubidium metaniobate and cesium metaniobate.

For the purpose of studying some of the properties of alkali metal metaniobates, we also prepared the metaniobates of lithium, sodium and potassium by the previously described methods [1, 10, 11]. Analytical results are set forth below.

Analysis of lithium metaniobate.
Weights of samples 0.2012 and 0.1930 g.
Found %: Nb_2O_5 90.10, 90.18; Li_2O 10.00, 9.96. $LiNbO_3$. Calculated %: Nb_2O_5 89.90; Li_2O 10.10.

Analysis of sodium metaniobate.

Weights of samples 0.2010 and 0.1996 g.
Found %: Nb_2O_5 81 12, 81.20; Na_2O 19.12, 19.28. $NaNbO_3$. Calculated %: Nb_2O_5 80.74; Na_2O 19.26.

Analysis of potassium metaniobate.

Weights of samples 0.2002 and 0.1973 g.

Found %: Nb_2O_5 74.20, 74.44; K_2O 25.98, 25.88. $KNbO_3$. Calculated %: Nb_2O_5 73.89; K_2O 26.11.

Thermal Stability and Volatility of Metaniobates of the Alkali Metals

Lithium, sodium and potassium metaniobates have high melting points and are evidently thermally stable substances. We investigated the thermal stability and volatility of all the anhydrous metaniobates prepared in this research.

The volatility was determined in an open crucible furnace at a temperature of 1200°. The first experiments showed that none of the investigated salts was volatile when heated for 2 and 6 hours; continuous heating was therefore applied for 24 hours at the same temperature. As in the preceding experiments, no losses in weight were found.

It may be mentioned that the metaniobates of lithium, potassium and cesium were melted at 1200° and retained their color unchanged.

Due to the lack of volatility of these salts even on prolonged heating, we carried out experiments for determination of their volatility in vacuum.

Volatility determinations were carried out at 1200° and a pressure of about 1 mm. The data obtained show that even under these conditions none of the salts is volatile.

Lowering of the pressure does not affect the thermal stability of metaniobates of the alkali metals. The thermal stability of metaniobates of the alkali metals can probably be accounted for by the ionic bond and by the stability of the NbO_3^{-1} ion [12]. The oxygen atoms of this ion are firmly anchored to the central atom and evidently do not manifest a tendency to polarize the ions of the alkali elements. All the metaniobates of the alkali metals are sparingly soluble in water.

TABLE

Equivalent and Specific Electrical Conductivities of Saturated Aqueous Solutions of Metaniobates of the Alkali Metals at 25°

(Cell constant 0.4439)

Compound	Electrical conductivity	
	Equivalent	Specific
$LiNbO_3$	$1.01 \cdot 10^{-4}$	$4,50 \cdot 10^{-5}$
$NaNbO_3$	$6,41 \cdot 10^{-5}$	$2,82 \cdot 10^{-5}$
$RbNbO_3$	$7.70 \cdot 10^{-5}$	$3,31 \cdot 10^{-5}$
$CsNbO_3$	$1,11 \cdot 10^{-4}$	$4.93 \cdot 10^{-5}$

We measured the equivalent and specific electrical conductivities of solutions saturated at 25°. The results are set forth in the Table

SUMMARY

1. Anhydrous metaniobates of rubidium and cesium were synthesized for the first time.

2. A study of the thermal stability of all the metaniobates of the alkali metals showed that all these salts are thermally stable at a temperature of 1200°.

3. Causes of the stability of the compounds in question were discussed.

4. Measurements were made of the equivalent and specific electrical conductivities of saturated solutions of metaniobates of the alkali metals.

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ANHYDROUS METANIOBATES AND METATANTALATES OF THE ALKALI METALS

II. METANTANTALATES OF THE ALKALI METALS

M. A. Pchelkina and A. V. Lapitsky

Very little information has been published about the anhydrous metatantalates of the alkali metals. Up to now only the metatantalates of sodium and potassium have been described [1]. We have synthesized the anhydrous metatantalates of the alkali metals and have studied some of their properties.

EXPERIMENTAL

Starting Substances

Tantalum pentoxide. Pure tantalum pentoxide was prepared from potassium fluorotantalate [2]. The crystalline precipitate (washed free from mother liquor) of sparingly soluble potassium fluorotantalate was recrystallized from 2% hydrofluoric acid solution, transferred to a lead dish and treated with concentrated sulfuric acid until completely decomposed. The slurry-like mass was washed into a large porcelain beaker, water was poured over it, and the tantalum pentoxide was thereby largely peptized by the sulfuric acid. To avoid the passage of the tantalum pentoxide into solution, the contents of the beaker were neutralized with ammonium hydroxide. The voluminous white precipitate of tantalum pentoxide was washed on the filter with 5% ammonium carbonate solution until disappearance of sulfate ion from the wash water. The tantalum pentoxide purified in this way was sufficiently pure.

Carbonates of alkali metals. The lithium carbonate was the chemically pure grade. The carbonates of rubidium and cesium used for preparation of tantalates have already been described by us [2].

Preparation of Anhydrous Metatantalates of Lithium, Rubidium and Cesium

After igniting at 800°, the pure tantalum pentoxide was finely pulverized and stirred with equimolar amounts of carbonates of lithium, rubidium and cesium. The prepared mixtures were placed in platinum crucibles (the mixture containing lithium carbonate was placed in a corundum crucible). Sintering was carried out in a crucible furnace at 800° for 4 hours. Attainment of constant weight was taken as the criterion of completion of the reaction. Even though we took a very small excess of the carbonate of the alkali metal, it was nevertheless necessary to remove its residues. It is known that reaction of tantalum pentoxide with excess of alkali metal carbonate can lead to formation also of soluble tantalates which pass into solution when the metatantalates are treated with water.

The metatantalates were treated with distilled water, washed with 2% acetic acid solution, dried, and ignited. Analyses, carried out for content of tantalum pentoxide and alkali metal oxide, determined as sulfate [2], showed that we had actually obtained the anhydrous metatantalates of lithium, rubidium and cesium. Below we set forth the results of the analyses of the prepared salts.

Analysis of lithium metatantalate.

Weights of substance 0.2020 and 0.2026 g.
Found %: Ta_2O_5 94.02, 93.98; Li_2O 5.84, 6.12. $LiTaO_3$. Calculated %: Ta_2O_5 93.68; Li_2O 6.44.

Analysis of rubidium metatantalate.

Weights of substance 0.2028 and 0.1916 g.
Found %: Ta_2O_5 71.08, 71.12; Rb_2O 28.81, 28.88. $RbTaO_3$. Calculated %: Ta_2O_5 70.83; Rb_2O 29.17.

Analysis of cesium metatantalate.

Weights of substance 0.1822 and 0.1618 g.
Found %: Ta_2O_5 60.82, 61.18; Cs_2O 39.04, 39.16. $CsTaO_3$. Calculated %: Ta_2O_5 61.05; Cs_2O 38.94.

As in the case of metaniobates, we decided to investigate the thermal stability of the metatantalates of the alkali metals. For this purpose we prepared the anhydrous metatantalates of sodium and potassium by the method which has been frequently described [1].

The method used was entirely identical with that described for the synthesis of the metatantalates of lithium, rubidium and cesium. We analyzed the prepared metatantalates of sodium and potassium for their content of tantalum pentoxide and alkali metal oxide.

Analysis of sodium metatantalate.

Weights of substance 0.2010 and 0.2020 g.
Found %: Ta_2O_5 88.36, 88.57; Na_2O 11.01, 11.38. $NaTaO_3$. Calculated %: Ta_2O_5 88.38; Na_2O 11.62.

Analysis of potassium metatantalate.

Weights of substance 0.2026 and 0.2018 g.
Found %: Ta_2O_5 81.98, 82.32; K_2O 17.96, 17.64. $KTaO_3$. Calculated %: Ta_2O_5 82.43; K_2O 17.57.

Thermal Stability and Volatility of the Metatantalates of the Alkali Metals

Preliminary examination of the properties of the metatantalates showed that the latter had high melting points; it could therefore be surmised that their thermal stability was high.

The conditions under which the thermal stability was determined were similar to those employed for the thermal stability determinations of metaniobates.

TABLE 1

Effect of the Bond Character on the Melting Point of the Oxide and Its Volatility at 1200°

Oxide	Melting point	Loss in weight after 24 hours' ignition (in %)
MoO_3	795°	2.3
WO_3	1473	0.08
Nb_2O_5	1520	None
Ta_2O_5	1470	None

TABLE 2

Melting Point of Alkali Metal Salts of Molybdic, Tungstic, Niobic, and Tantalic Acids

Anion / Cation	Melting point			
	NbO_3^{-1}	MoO_4^{-2}	TaO_3^{-1}	WO_4^{-2}
Li^{+1}	1164	705° [4]	>1200°	742° [3]
Na^{+1}	~1250	687	>1200	698
K^{+1}	1184	926	>1200	926
Rb^{+1}	~1200	929	>1200	959
Cs^{+1}	>1200	925	>1200	958

TABLE 3

Volatility of Niobates, Molybdates, Tantalates and Tungstates of the Alkali Metals at 1200° after 24 hours, expressed as %

Anion / Cation	NbO_3^{-1}	MoO_4^{-2}	TaO_3^{-1}	WO_4^{-2}
Li^{+1}	None	0.73 [4]	None	0.43 [5]
Na^{+1}		1.84		0.25
K^{+1}		6.38		2.49
Rb^{+1}		11.92		5.72
Cs^{+1}		29.15		28.12

TABLE 4

Equivalent and Specific Electrical Conductivities of Aqueous Solutions of Metatantalates of the Alkali Metals at 25°
(Cell constant 0.4439)

Compound	Electrical conductivity	
	Equivalent	Specific
$LiTaO_3$	$8.81 \cdot 10^{-5}$	$3.91 \cdot 10^{-5}$
$NaTaO_3$	$5.90 \cdot 10^{-5}$	$2.62 \cdot 10^{-5}$
$KTaO_3$	$7.61 \cdot 10^{-5}$	$3.28 \cdot 10^{-5}$
$RbTaO_3$	$7.55 \cdot 10^{-5}$	$3.25 \cdot 10^{-5}$
$CsTaO_3$	$6.08 \cdot 10^{-5}$	$2.70 \cdot 10^{-5}$

Results of ignition of all the anhydrous alkali metatantalates show that they do not possess appreciable volatility at a temperature of 1200°.

We also investigated the volatility of the same salts at the same temperature but in vacuum. The pressure in the apparatus was about 1 mm.

The duration of heating in this series of experiments was 2 and 6 hours. In all cases we found no change in weight of the metatantalates of the alkali metals.

The constancy of weight points to the thermal stability of all the salts and to the absence of volatility even in vacuum at 1200°. It should be mentioned that under these conditions the metatantalates do not melt and their color remains unchanged.

The thermal stability of metatantalates of the alkali elements may be explained by the bond strength of the TaO_3^{-1} ion. The oxygen ions, rigidly linked to the central tantalum atom, evidently do not exert a polarizing action on the alkali metal ions.

Our data for the thermal stability of anhydrous metaniobates and metatantalates of the alkali metals show that these compounds (with high melting temperatures of 1200° or higher) are lacking in volatility, evidently due to the ionic character of the bond[6].

It is interesting to compare the melting point and volatility of some compounds of molybdenum, tungsten, niobium and tantalum. Comparison of these values (Table 1), found for the oxides by Spitsyn and Shostak [3], shows that volatility is manifested by oxides of molybdenum and tungsten which have a less marked ionic character of bond than the oxides of niobium and tantalum.

The same picture is observed for salts of molybdic, tungstic, niobic and tantalic acids, as seen from the data set forth in Tables 2 and 3.

The lessening of the ionic character of the bond with gradual transition to a polar bond is usually associated with a decrease in the melting point of the salts and an increase in their volatility.

On the basis of the above facts, we may say that passage from niobates to molybdates and from tantalates to tungstates is accompanied by a change from an ionic to a polar character of bond.

Like the anhydrous alkali metal metaniobates, the corresponding metatantalates are sparingly soluble in water. We determined the equivalent and specific electrical conductivities of solutions of all the metantalates of the alkali metals saturated at 25°. Results of the measurements are set forth in Table 4. The results obtained bear a qualitative character.

The actual solubilities of these salts can only be obtained after determination of the mobility of the metatantalate ion or by the method of radioactive indicators.

SUMMARY

1. Anhydrous metatantalates of lithium, rubidium and cesium were prepared for the first time.

2. The thermal stability of all the anhydrous alkali metal metatantalates was studied; it was established that all these salts are thermally stable at 1200°.

3. The melting points of the metaniobates, molybdates, metatantalates and tungstates of the alkali metals were compared. Considerations about the causes of the stability of metaniobates and metatantalates of the alkali metals are put forward.

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PREPARATION OF THE SIMPLEST SODIUM CUPROTHIOSULFATES

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The literature contains descriptions of salts with fairly diverse molar ratios of $Cu_2S_2O_3$, $Na_2S_2O_3$ and crystal water [4, 5, 7-10, 12, 13]. The following salts are also known:

$$3Cu_2S_2O_3 \cdot 2Na_2S_2O_3 \cdot 2NaCl \cdot 8H_2O\ [6],$$
$$5Cu_2S_2O_3 \cdot 3Na_2S_2O_3 \cdot 2Na_2SO_4\ [8] \text{ and}$$
$$9Cu_2S_2O_3 \cdot 5Na_2S_2O_3 \cdot 8NaCl \cdot 12H_2O\ [9].$$

Rosenheim and Steinhauser [12] isolated the salts:

$$4Cu_2S_2O_3 \cdot 3Na_2S_2O_3 \cdot 6H_2O,\ Cu_2S_2O_3 \cdot Na_2S_2O_3 \cdot 2H_2O \text{ and } 5Cu_2S_2O_3 \cdot 4Na_2S_2O_3 \cdot 8.5H_2O.$$

They also described more complex salts, for example:

$$4(NH_4)_2S_2O_3 \cdot NH_4X \cdot CuX \quad (\text{where: } X = Cl'; Br'; I'; CNS'),$$

to which Werner assigned the structure $(NH_4)_9[Cu(S_2O_3)_4X_2]$. Benrath [14] isolated a dark-blue salt $Cu_2S_2O_3 \cdot 2Na_2S_2O_3 \cdot 5NH_3$. Potassium salts known are $K_5[Cu(S_2O_3)_3] \cdot 3H_2O$ and $K_7[Cu(S_2O_3)_4]$, which were isolated by Spacu and Murgulescu [15], and whose existence was denied by Ryabchikov on the grounds that a maximum of two thiosulfate residues can surround one atom of copper [1]. A paper by Ryabchikov and Silnichenko [2], indicated that the varying composition of the salt is due both to faulty conception of the mechanism of the reaction, in which, for the most part, no account was taken of the formation of an intermediate salt of $Cu_2S_2O_3$, and to the special characteristics of complex formation of copper compounds. According to the hypothesis advanced, only three types of complex salts must exist: $Me[Cu(S_2O_3)]$, $Me_4[Cu_2(S_2O_3)_3]$ and $Me_3[Cu(S_2O_3)_2]$ with a coordination number of copper equal to 2. It was also observed that the properties of the salt $NaCuS_2O_3$ do not correspond to the properties described by other investigators. Thus, with ratios of copper sulfate to sodium thiosulfate of 1:2, a green solution is formed which contains the readily water-soluble salt $NaCuS_2O_3$. To the yellow salt which is sparingly soluble in water is assigned the structure $CuNa_2$-$[Cu(S_2O_3)_2]$ [2]. The latter was obtained by adding a saturated solution of copper sulfate to a saturated solution of sodium thiosulfate until the colorless solution turned green (i.e., as in the formation of the salt $NaCuS_2O_3 \cdot H_2O$). Finally, the preparation of this salt according to the equation

$$CuNa_2[Cu(S_2O_3)_2] + 2\,Na_2S_2O_3 \rightarrow 2Na_3[Cu(S_2O_3)_2].$$

is unconvincing as a confirmation of the composition of the salt $CuNa_2[Cu(S_2O_3)_2]$, since this reaction also takes place with 2 moles of the salt $NaCuS_2O_3$.

Since data for the composition and properties of the simplest sodium cuprothiosulfates are still conflicting, we decided to start this investigation. The literature describes the salt $NaCuS_2O_3 \cdot H_2O$ and water-insoluble, poorly stable salts with a yellow color: $Cu_2S_2O_3 \cdot K_2S_2O_3 \cdot H_2O$ or $KCuS_2O_3 \cdot H_2O$ and $Cu_2S_2O_3 \cdot (NH_4)_2S_2O_3 \cdot 2H_2O$ or $NH_4CuS_2O_3 \cdot H_2O$.

Due to the varying valence of copper in the reaction of copper sulfate with sodium thiosulfate [11], when preparing the salt $NaCuS_2O_3$ it is necessary to take them in the ratio of 1:2.

$$\begin{array}{l} 2CuSO_4 + 3Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + 2Na_2SO_4 + Na_2S_4O_6 \\ Cu_2S_2O_3 + Na_2S_2O_3 \rightarrow 2NaCuS_2O_3 \\ \hline 2CuSO_4 + 4Na_2S_2O_3 \rightarrow 2NaCuS_2O_3 + 2Na_2SO_4 + Na_2S_4O_6 \end{array}$$

Since the required salt is sparingly soluble in water, its yield must be close to the theoretical. On starting, however, from a 1:1 ratio, the yield of $NaCuS_2O_3$ must be nearly halved.

The salt $Na_3[Cu(S_2O_3)_2]$ was prepared by us both directly, from copper sulfate, and from the salt $NaCuS_2O_3 \cdot H_2O$. In the former case the starting components will be taken in the ratio of 1:3.

$$\begin{array}{l} 2CuSO_4 + 3\,Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + 2Na_2SO_4 + Na_2S_4O_6 \\ Cu_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3[Cu(S_2O_3)_2] \\ \hline 2CuSO_4 + 6Na_2S_2O_3 \rightarrow 2Na_3[Cu(S_2O_3)_2] + 2Na_2SO_4 + Na_2S_4O_6 \end{array}$$

In the second case the reaction proceeds according to the equation: $NaCuS_2O_3 + Na_2S_2O_3 \rightarrow Na_3[Cu(S_2O_3)_2]$.

Since in the second case no by-products of the reaction are formed and the volume of reaction solution is very small, separation of the reaction product proceeds considerably more easily, the yields are better, and a purer salt is obtained. In both cases, however, precipitation with alcohol leads to formation of an oily reaction product. For this reason the isolation of the product is preferably effected by precipitation with alcohol in association with salting-out with sodium nitrate. The salt $Na_3[Cu(S_2O_3)_2]$ is fairly stable in comparison with $NaCuS_2O_3 \cdot H_2O$ and the crystal water can be removed by drying at 90-95°. In aqueous solutions it decomposes after storing for many hours or (especially) on heating above 50°.

The salt $Na_3[Cu(S_2O_3)_2]$ is adequately stable in a saturated aqueous solution of sodium thiosulfate both at room temperature and when heated to 60°. Both this observation and work on the salt of silver of analogous composition [3] served us as a basis for preparation of the salts $Na_5[Cu(S_2O_3)_3]$, $Na_7[Cu(S_2O_3)_4]$ and $Na_9[Cu(S_2O_3)_5]$. These were prepared according to the equations:

$$NaCuS_2O_3 + 2Na_2S_2O_3 \rightarrow Na_5[Cu(S_2O_3)_3],$$
$$NaCuS_2O_3 + 3Na_2S_2O_3 \rightarrow Na_7[Cu(S_2O_3)_4],$$
$$NaCuS_2O_3 + 4Na_2S_2O_3 \rightarrow Na_9[Cu(S_2O_3)_5].$$

Aqueous solutions of these salts possess adequate stability in storage and when heated. Crystallization may occur in the solutions. The crystals are readily dehydrated, losing their water at 85-90°. By comparison with $NaCuS_2O_3$ and $Na_3[Cu(S_2O_3)_2]$ they are much more stable. Thus, their aqueous solutions can be kept for several weeks without visible signs of decomposition, and they also resist heating to 80-90°. Of these three salts the least stable is $Na_5[Cu(S_2O_3)_3]$, and during its preparation it is therefore necessary to take a slight excess of sodium thiosulfate.

The composition of these three salts was verified by the preparation from them of the barium salts, and also the salt $Ba_3[Cu(S_2O_3)]_2$:

$$2Na_3[Cu(S_2O_3)_2] + 3BaCl_2 \rightarrow Ba_3[Cu(S_2O_3)_2]_2 + 6NaCl,$$
$$2Na_5[Cu(S_2O_3)_3] + 5BaCl_2 \rightarrow Ba_5[Cu(S_2O_3)_3]_2 + 10NaCl,$$
$$2Na_7[Cu(S_2O_3)_4] + 7BaCl_2 \rightarrow Ba_7[Cu(S_2O_3)_4]_2 + 14NaCl,$$
$$2Na_9[Cu(S_2O_3)_5] + 9BaCl_2 \rightarrow Ba_9[Cu(S_2O_3)_5]_2 + 18NaCl.$$

These barium salts are sparingly soluble in water (about 1:3000), whereas the solubility of BaS_2O_3 is 1:480 (20°); therefore for titration with iodine a weighed sample of about 0.2 g is dissolved in 800 ml water with vigorous stirring for one to one and a half hours. The amount of potassium iodide taken is calculated on the basis of 4 g per 100 g solution; this avoids development of cloudiness toward the end of the addition of iodine and ensures stability of the blue color of the solution.

The barium salts resemble the sodium salts in respect of stability on keeping and heating.

EXPERIMENTAL*

Preparation of Sodium cuprothiosulfate $NaCuS_2O_3 \cdot H_2O$.

To 10 g $CuSO_4 \cdot 5H_2O$ dissolved in 50 ml water was added a solution of 20 g $Na_2S_2O_3 \cdot 5H_2O$ in 10 ml water until the blue color of the reaction solution changed to green, whereupon without delay about 1 ml 20% copper sulfate solution was run in to give a persistent green color. Formation of a yellow precipitate was accelerated by stirring. By the next day its amount had considerably increased and it was separated, washed 3 times with mother liquor diluted 1:1 with water (without allowing loss of crystals from the liquid), 3 times with the minimum amount of water, 5 times with 50% alcohol and 5 times with alcohol. Thorough washing improves the keeping quality of the crystals. Stability in storage depends upon the temperature. When the yellow crystals are kept in a refrigerator at 0-2°, their color does not change in the course of about 4 months. The weight of the air-dry precipitate was 7.7 g (89%). Drying of the crystals at 50-60° for only 30-40 minutes leads to their decomposition.

0.1910, 0.2560 g sub.: 8.8, 11.6 ml 0.1 N I_2. 0.2020, 0.2076 g sub.: 9.8, 10.0 ml 0.1 N $Na_2S_2O_3$.
Found %: S_2O_3 51.5, 50.6; Cu 30.8, 30.7. $NaCuS_2O_3 \cdot H_2O$. Calculated %: S_2O_3 51.8; Cu 29.4.

Preparation of sodium cuprodithiosulfate $Na_3[Cu(S_2O_3)_2]$.

5 g $CuSO_4 \cdot 5H_2O$ in 20 ml water was added to a solution of 15 g $Na_2S_2O_3 \cdot 5H_2O$ in 10 ml water. Into the filtered solution was introduced 7 g sodium nitrate dissolved by stirring. 60 ml alcohol was added in portions and

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* E. Ya. Karaulova participated in the analytical work.

on stirring a snow-white precipitate came down.

It was separated the next day, washed with alcohol and stirred with 70% alcohol, using not more than 60 ml of alcohol (excess of the latter results in a viscous mass). The precipitate was separated and washed, first with 70% alcohol until the test for nitrate was negative (test with diphenylamine), and again with alcohol. After drying in air with gradual rise of temperature from 50 to 90-95°, the weight of the precipitate was 5.3 g (66.5%).

0.1580, 0.1760 g sub.: 8.8, 9.9 ml 0.1 N I_2. 0.2046, 0.2201 g sub.: 5.4, 6.0 ml 0.1 N $Na_2S_2O_3$. Found %: S_2O_3 62.4, 62.8; Cu 16.8, 17.3. $Na_3[Cu(S_2O_3)_2]$. Calculated %: S_2O_3. 63.0; Cu 17.85.

If the reaction product was separated with alcohol in the absence of sodium nitrate, an oily layer was formed which was collected and poured into a crystallizing dish after mixing with a fresh portion of alcohol. After 48 hours white crystals had formed and these were separated and mixed with alcohol (it was impossible to wash them with alcohol since a thick crust formed on the surface of the precipitate), again separated, and washed with alcohol.

Addition to 5 g $Na_2SO_3 \cdot 5H_2O$ in 5 ml water of 4.3 g $NaCuS_2O_3 \cdot H_2O$ with stirring gave a reaction solution from which, after working up in the above-described way, was separated a salt of the same composition $Na_3[Cu(S_2O_3)_2]$. To 1 g $Na_3[Cu(S_2O_3)_2]$, dissolved in 5 ml water, was added 30 ml 5% $BaCl_2$ solution. The resultant snow-white precipitate was separated, washed with water until the reaction for chlorine ion was negative and washed 5 times with alcohol. The snow-white crystals of $Ba_3[Cu(S_2O_3)_2]_2$ were dried to constant weight at 90-95°.

0.1840, 0.1920 g sub.: 0 1280, 0.1360 g $BaSO_4$. 0.2180, 0.2220 g sub.: 4.0, 4.2 ml 0.1 N. $Na_2S_2O_3$. 0.1840, 0.2040 g sub.: 7.3, 8.2 ml 0.1 N. I_2. Found %: Ba 40.8, 41.7; Cu 12.4, 12.0; S_2O_3 44.4, 44.9. $Ba_3[Cu(S_2O_3)_2]_2$. Calculated %: Ba 41.7; Cu 12.88; S_2O_3 45.5.

Preparation of sodium tricuprothiosulfate $Na_5[Cu(S_2O_3)_3]$

To a solution of 25 g $Na_2S_2O_3 \cdot 5H_2O$ in 15 ml water was added portionwise with stirring 10.8 g $NaCuS_2O_3 \cdot H_2O$ until completely dissolved. The solution was evaporated at 40° and then in succession at 50, 60 and 80° until a precipitate had been obtained either in the form of a thick slurry or of a solid. The precipitate was dissolved in the minimum amount of water and filtered, and the water removed in the manner described above. After drying to constant weight at 90-95° the precipitate weighed 23.5 g (90%).

0.2355, 0.2353 g sub.: 4.4, 4.3 ml 0.1 N $Na_2S_2O_3$. 0.1940, 0.1787 g sub.: 11.2, 10.4 ml 0.1 N I_2. Found %: S_2O_3 64.6, 65.1; Cu 11.8, 11.65. $Na_5[Cu(S_2O_3)_3]$. Calculated %: S_2O_3 65.4; Cu 12.35.

The barium salt was prepared from a 10% solution of $Na_5[Cu(S_2O_3)_3]$ and a 5% solution of $BaCl_2$ taken in the stoichiometric ratio.

0.2146, 0.2090 g sub.: 0.1650, 0.1630 g $BaSO_4$. 0.1620, 0.1650 g sub.: 2.2, 2.3 ml 0.1 N $Na_2S_2O_3$. 0.2006, 0.3043 g sub.: 8.0, 12.0 ml 0.1 N I_2. Found %: Ba 45.3, 45.9; Cu 8.9, 8.8; S_2O_3 44.7, 44.0. $Ba_5[Cu(S_2O_3)_3]_2$. Calculated %: Ba 46.2; Cu 8.55; S_2O_3 45.3.

Preparation of sodium tetracuprothiosulfate $Na_7[Cu(S_2O_3)_4]$.

To a solution of 11.25 g $Na_2S_2O_3 \cdot 5H_2O$ in 6 ml water was added 3.24 g $NaCuS_2O_3 \cdot H_2O$. The conditions for carrying out the reaction and for isolation of the product were the same as for $Na_5[Cu(S_2O_3)_3]$. Weight of salt 8 g (80%).

0.3214, 0.2434 g sub.: 18.9, 14.5 ml 0.1 N I_2. 0.2622, 0.1982 g sub.: 4.1, 3.1 ml 0.1 N $Na_2S_2O_3$. Found %: S_2O_3 65.8, 66.7; Cu 9.92, 9.93. $Na_7[Cu(S_2O_3)_4]$. Calculated %: S_2O_3 66.8; Cu 9.45.

The barium salt was prepared in the same way as for $Ba_5[Cu(S_2O_3)_3]_2$.

0.2880, 0.2680 g sub.: 0.2323, 0.2160 g $BaSO_4$. 0.1888, 0.2680 g sub.: 1.9, 2.6 ml 0.1 N $Na_2S_2O_3$. 0.1988, 0.2080 g sub.: 7.9, 8.0 ml 0.1 N I_2. Found %: Ba 47.4, 47.5; Cu 6.4, 6.1; S_2O_3 44.5, 44.1. $Ba_7[Cu(S_2O_3)_4]_2$. Calculated %: Ba 48.33; Cu 6.4; S_2O_3 45.1.

Preparation of sodium pentacuprothiosulfate $Na_9[Cu(S_2O_3)_5]$.

To a solution of 15 g $Na_2S_2O_3 \cdot 5H_2O$ in 7 ml water was added 3.24 g $NaCuS_2O_3 \cdot H_2O$. The conditions for carrying out the reaction and for separating the product were the same as for $Na_5[Cu(S_2O_3)_3]$. After drying to constant weight the crystals weighed 11.6 g (94.5%).

0.3095, 0.3200 g sub.: 18.3, 19.0 ml 0.1 N I_2. 0.2440, 0.2660 g sub.: 2.7, 2.8 ml 0.1 N $Na_2S_2O_3$. Found %: S_2O_3 66.2, 66.4; Cu 7.0, 6.7. $Na_9[Cu(S_2O_3)_5]$. Calculated %: S_2O_3 67.4; Cu 7.65.

The barium salt was prepared as described for $Ba_5[Cu(S_2O_3)_3]_2$.

0.3020, 0.2820 g sub.: 0.2520, 0.2340 g $BaSO_4$. 0.1930, 0.2306 g sub.: 1.4, 1.8 ml 0.1 N $Na_2S_2O_3$. 0.2010, 0.2002 g sub.: 8.0, 7.9 ml 0.1 N I_2. Found %: Ba 49.2, 48.8; Cu 4.6, 4.97; S_2O_3 44.5, 44.1. $Ba_9[Cu(S_2O_3)_5]_2$. Calculated %: Ba 49.72; Cu 5.12; S_2O_3 45.08.

SUMMARY

1. The methods for preparation of $NaCuS_2O_3 \cdot H_2O$ and $Na_3[Cu(S_2O_3)_2]$ have been improved.

2. Methods are presented for preparation of the previously undescribed salts: $Na_5[Cu(S_2O_3)_3]$, $Na_7[Cu(S_2O_3)_4]$, $Na_9[Cu(S_2O_3)_5]$, $Ba_3[Cu(S_2O_3)_2]_2$, $Ba_5[Cu(S_2O_3)_3]_2$, $Ba_7[Cu(S_2O_3)_4]_2$ and $Ba_9[Cu(S_2O_3)_5]_2$.

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REACTIONS IN SOLUTIONS BETWEEN ZIRCONIUM NITRATE AND ALKALI METAL IODATES. I.

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Composition of freshly precipitated zirconium iodate. The first publication on the composition of zirconium iodate was that of Davis [1] who prepared zirconium oxyiodates of indeterminate composition. Venable and Smithey [2] also separated precipitates of indeterminate composition [between $Zr_2O_4(IO_3)_4$ and $Zr_4O_7(IO_3)_2$]. They suggested that they did not isolate the normal zirconium iodate [$ZrO(IO_3)_2$] because this salt is strongly hydrolyzed when washed with water.

In 1941 Chemikov and Uspenskaya [3] reported that precipitation of zirconium from nitrate solutions gives iodates of variable composition. According to their data, one can also obtain precipitates of definite composition, for example

$$2Zr(IO_3)_4 \cdot KIO_3 \cdot 8H_2O,$$

by strictly adhering to the conditions established by them. On this basis the authors recommended a volumetric iodometric method of determination of zirconium.

Handbooks [4] report that on standing of zirconium iodate precipitates with the mother liquors for a long time, compounds are formed which contain 7.5 to 9 iodate groups per atom of zirconium. No indication is given of the character and properties of such compounds.

It appears from the literature data that the study of the composition of zirconium iodate precipitates has been inadequate. No systematic investigations have been undertaken, so that it is difficult to judge the correctness of existing data for the composition of zirconium iodate.

EXPERIMENTAL

Experimental method*. Use was made in the experiments of standard aqueous or nitric acid solutions of zirconium nitrate and potassium iodate. The precipitates of zirconium iodate were prepared by adding potassium iodate solution to zirconium nitrate solution. In some experiments dry potassium iodate was also added.

The number of iodate groups combining with zirconium was determined by analyzing the precipitates and by back-titration.

To an accurately measured volume of standard zirconium nitrate solution was added an accurately measured volume of standard (in respect of IO_3) potassium iodate solution. The resultant precipitate (fresh or after standing) was separated from the mother liquor. The mother liquor was collected separately from the wash waters. An aliquot portion of the mother liquor was taken for determination of iodate ions which had not reacted with zirconium. The iodometric method was employed.

From the difference between the amount of potassium iodate (iodate ions) taken and the amount remaining in solution, the amount of iodate which had reacted with zirconium was determined. The fall in the iodate ion content of the solution was related to the amount of zirconium isolated in the precipitate. Similar calculations can also be based on data for the fall in concentration of iodate ions and of zirconium in solution due to formation of zirconium iodate.

The precipitate was washed with water, or with alcohol and ether, or with acid, alcohol and ether, and it was then dried at room temperature. Zirconium and iodate groups were determined in weighed amounts of the air-dry precipitate. The analytical results gave the ratio between zirconium and iodate groups.

Comparison of the ratios between zirconium and iodate groups found by analysis of the precipitate with those determined by back-titration permitted evaluation of the suitability of the wash liquids tested.

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* The procedures described refer both to freshly brought-down precipitates and to those which have stood in contact with the mother liquors.

Back-titration was used by choice in experiments carried out with a large excess of added potassium iodate, when the zirconium came down quantitatively. When the zirconium did not come down completely, the results were corrected from determinations of the zirconium in the mother liquors.

On the basis of back titration,.3 N HNO_3 was selected as the wash liquid. Water and alcohol were found unsuitable.

After the precipitate had been separated by centrifuging, it was washed 5-6 times with wash liquid, 2-3 times with alcohol (95% by volume) and 2-3 times with ether. Washing with nitric acid completely eliminated the excess potassium iodate; the alcohol got rid of the nitric acid, and the ether removed the alcohol.

As was pointed out, the precipitates were analyzed for potassium, zirconium and iodate groups. In some precipitates the content of crystal water was also determined by drying at 90-95°, and also the nitrate content by Devarda's method under the conditions described by Hillebrand and Lendel [5]. For the latter analysis, instead of 2.5 g Devarda alloy, 4 g was taken to allow for its consumption for reduction of iodate to iodide.

Zirconium was determined in 400-500 mg precipitate; this was dissolved in 5 ml concentrated hydrochloric acid, diluted to about 100 ml with distilled water, and then the iodate was reduced to iodide with 30% hydroxylamine solution. After decomposition of the iodate, the zirconium was precipitated with ammonia and the precipitated hydrous oxide was, as usual, washed, ignited, and dried.

The potassium was determined in the filtrate from the zirconium hydroxide. The filtrate was first evaporated to a small volume in a beaker, and the residue of liquid was transferred to a weighed porcelain crucible and evaporated to dryness. The dry residue was dissolved in a small volume of distilled water, whereupon addition was made to the solution of 2-3 drops of 30% hydroxylamine solution. In the event of iodate being found in the dry residue (separation of free iodine), the treatment with hydroxylamine was repeated until the iodate had been entirely converted into hydriodic acid and it had been removed by evaporation from the hydrochloric acid solution.

The residual potassium chloride was ignited to constant weight, and the amount of potassium in the weighed sample of zirconium iodate precipitate taken was calculated. The potassium content was also determined by the chloroplatinate method.

The number of iodate groups entering into the composition of the precipitate was determined iodometrically on a 60-80 mg sample. The weighed sample of iodate precipitate in a weighing bottle was dissolved in 2.5 ml concentrated (or 5 ml 1:1 diluted) sulfuric acid (complete solution of the precipitate sometimes called for brief heating on a water bath). The sulfuric acid solution was diluted with water to 250 ml, 1 g dry potassium iodide was added, and the liberated iodine was titrated with an 0.05N (or slightly stronger) sodium thiosulfate solution in presence of starch. The titer of the thiosulfate was determined under the same conditions.

Numerical results of analysis of the zirconium iodate precipitates were obtained in not fewer than two experiments (in each case) carried out under identical conditions.

Compositions of precipitates of freshly precipitated zirconium iodates. The starting solution of zirconium nitrate contained 1.4 g zirconium per liter. All the experiments were carried out at room temperature, which varied between +15 and +25° Results are set forth in the table. When examining the tabulated data it must be remembered that at low concentrations of potassium iodate in the nitric acid solutions, the zirconium partly came down in the precipitate. The zirconium iodate has a variable composition, which changes with changing concentration of potassium iodate and with changing acidity. At low acidities of the solutions (pH 2-3) the potassium iodate concentration of the solution scarcely influenced the composition of the precipitate. Moniodate comes down both with large and small additions of potassium iodate (experiments 1-4). Only with very large excesses of potassium iodate in the solution was up to 1.3 iodate groups per atom of zirconium found in the precipitate (experiment 4), and this was evidently due to adsorption of potassium iodate by the voluminous precipitate of zirconium monoiodate.

If the acidity of the solution is not too low, the composition of the precipitates depends in the main on the excess of added potassium iodate. With low concentrations of potassium iodate, part of the zirconium present in the solution forms moniodate and is thereby brought down, while the other part remains in solution (experiments 5, 11, 15 and 21). The lower the acidity of the solution, the greater is the proportion of zirconium which may be brought down as monoiodate. The conditions under which zirconium is quantitatively brought down in the precipitate in the form of monoidate have been noted above.

On addition of a large excess of potassium iodate to nitric acid solutions of zirconium, only zirconium triiodate is detected in the precipitates. Formation of triiodate is observed over a wide range of acidities and excesses of added potassium iodate (experiments 10, 14, 18-20, 24 and 25).

By regulation of the excess of added potassium iodate it is possible to obtain from the nitric acid solutions precipitates of intermediate compositions with a content of more than one and less than three iodate groups per atom of

Composition of freshly precipitated zirconium iodates

Zirconium concentration in the final volume 0.00762 mole/liter (0.695 g/liter)

Experiment No.	Concentration of IO_3 (in g-ions/liter		Fall in concentration of IO_3 in solution (by difference)	Content in precipitate (in %)				Ratio of $Zr : IO_3 : H_2O$
	Before precipitation of the zirconium	After precipitation of the zirconium		Zr	IO_3	Total	H_2O (by difference)	
pH 2.25								
1	0.0097	0.0042	0.0055	22.93	46.07	69.00	31.00	1 : 1.05 : 6.83
2	0.064	0.0562	0.0078	22.32	47.10	69.42	30.58	1 : 1.10 : 6.94
3	0.107	0.097	0.010	20.91	48.93	69.84	30.16	1 : 1.28 : 7.31
4	0.161	0.152	0.009	20.68	50.89	71.57	28.43	1 : 1.28 : 6.97
0.07 N HNO_3								
5	0.008	0.0079	0.0001	23.27	41.68	65.95	35.05	1 : 0.93 : 7.63
6	0.024	0.010	0.014	16.60	63.99	80.59	19.41	1 : 2.01 : 5.92
7	0.050	0.032	0.018	14.61	68.23	82.84	17.16	1 : 2.43 : 5.95
8	0.077	0.056	0.021	13.71	69.24	82.95	17.05	1 : 2.63 : 6.30
9	0.111	0.089	0.022	13.65	74.12	87.77	12.23	1 : 2.83 : 4.54
10	0.152	0.129	0.023	13.51	76.06	89.57	10.43	1 : 2.94 : 3.91
0.5 N HNO_3								
11	0.0113	0.0070	0.0043	21.89	48.40	70.29	29.71	1 : 1.15 : 6.88
12	0.0206	0.0054	0.015	16.71	64.36	81.07	18.93	1 : 2.03 : 5.74
13	0.033	0.015	0.018	14.62	67.24	81.86	18.14	1 : 2.40 : 6.29
14	0.061	0.040	0.021	12.85	73.25	86.10	13.90	1 : 2.94 : 5.48
0.99 N HNO_3								
15	0.015	0.015	–	23.02	45.58	68.60	31.40	1 : 1.03 : 6.91
16	0.026	0.008	0.018	17.78	60.45	78.29	21.77	1 : 1.77 : 6.20
17	0.045	0.023	0.022	13.41	72.81	86.22	13.78	1 : 2.83 : 5.21
18	0.054	0.031	0.023	12.89	74.12	87.01	12.99	1 : 3.00 : 5.11
19	0.077	0.053	0.024	12.81	75.58	88.39	11.61	1 : 3.08 : 4.57
20	0.350	0.327	0.023	12.77	76.62	89.33	10.67	1 : 3.13 : 4.23
5 N HNO_3								
21	0.037	0.037	–	23.09	44.11	67.20	32.80	1 : 0.96 : 7.20
22	0.051	0.035	0.016	15.02	67.14	82.16	17.84	1 : 2.33 : 5.73
23	0.059	0.014	0.019	13.30	74.08	87.38	12.62	1 : 2.90 : 4.81
24	0.086	0.063	0.023	12.90	76.06	88.96	11.04	1 : 3.07 : 4.34
25	0.571	0.547	0.024	12.70	76.29	88.99	11.01	1 : 3.13 : 4.39

zirconium. The majority of these precipitates are evidently mixtures into which, in particular, enter zirconium monoiodate and triiodate. When a very high concentration of potassium iodate is formed in the solution, a portion of the zirconium (still in solution) forms triiodate, and at the same time other precipitates which react with the potassium iodate present in solution are also transformed into triiodate. Consequently, when zirconium is precipitated from very weakly acidic solutions, the stable precipitates are monoiodates, while on precipitation from solutions containing a considerable amount of acid the stable precipitates are triiodates.

Stable precipitates of zirconium tetraiodate are not formed, at least not at acidities up to 7.5 N and with any given concentration of potassium iodate in solution. Potassium and nitrate groups do not enter into the composition of iodates which have been freshly precipitated and left for short periods (1-1½ hours). Consequently the freshly precipitated zirconium iodates are hydroxy compounds. The moniodate and triiodate can be dried to constant weight at 90-95°; during the operation the precipitates turn slightly brown, indicating partial breakdown at these temperatures. The loss of weight of the moniodate during drying corresponds to the removal of 4.25 to 4.40 molecules water; that of the triiodate to 3.90-4.10 molecules.

Taking into consideration the difficulties resulting from partial decomposition of zirconium iodates during drying, we may assume that the monoiodate and triiodate each contain 4 molecules of crystal water. Experiments 1-4, 11, 15 and 21 show that in air-dry samples of zirconium monoiodate the total content of zirconium and iodate groups is 69-70%; the remaining 31-30% corresponds to a content of roughly 7 molecules of water (or 3 hydroxyl groups, which are not lost on drying, and 4 molecules of water which are lost at 90-95°). In the triiodate the over-all content of zirconium and iodate groups is 88%.

On the basis of the analytical data, the composition of zirconium monoiodate may be represented by $Zr(OH)_3IO_3 \cdot 4H_2O$, and that of the triiodate by $ZrOH(IO_3)_3 \cdot 4H_2O$.

Zirconium diiodate was not isolated, although it is reasonable to assume that it exists and comes down from nitric acid solutions after precipitation of the monoiodate. Zirconium diiodate must have the following composition: $Zr(OH)_2(IO_3)_2 \cdot 4H_2O$. When a large excess of potassium iodate is added, the diiodate (like the monoiodate) changes into triiodate.

SUMMARY

1. Addition of potassium iodate to a solution of zirconium nitrate causes precipitation of a hydroxy compound containing from one to three iodate groups per atom of zirconium. The amount of combining iodate ions depends upon the amount of added potassium iodate as well as on the acidity of the solution. When potassium iodate is used as the precipitant, zirconium does not form stable precipitates of tetraiodate.

2. When zirconium is precipitated from an aqueous solution of its nitrate with an aqueous solution of potassium iodate (pH of the mixture of solutions 2-3) the monoiodate $Zr(OH)_3IO_3 \cdot 4H_2O$ is formed. The composition of the precipitates changes somewhat with a large excess of potassium iodate in the solution, probably due to adsorption of potassium iodate.

3. Zirconium comes down from nitric acid solutions in the form of an iodate of variable composition. When a small amount of potassium iodate is added, part of the zirconium comes down as the monoiodate with composition as above. When a large excess of potassium iodate is added, only the triiodate $ZrOH(IO_3)_3 \cdot 4H_2O$ is detected in the precipitate.

By regulating the excess of added potassium iodate, it is possible to obtain precipitates with intermediate compositions containing more than one and less than three iodate groups per atom of zirconium.

4. Zirconium triiodate is formed from zirconium nitrate as well as from precipitates of hydroxyiodates containing fewer than three iodate groups per atom of zirconium. In the latter case, the hydroxyl groups (all but one) are replaced by iodate groups. Zirconium triiodate is formed over wide intervals of acidities and of concentrations of potassium iodate in the solution.

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REACTION OF BARIUM TITANATE WITH FLUORIDES AND PYROPHOSPHATES OF SODIUM AND POTASSIUM

M.L. Sholokhovich and I.N. Belyaev

Sodium fluorides and pyrophosphates are some of the best solvents for barium titanate in melts [1]. For this reason the investigation of the reaction of $BaTiO_3$ with these salts in melts is a matter of special interest both for the purposes of growing single crystals of $BaTiO_3$ from molten media and for clarification of the mechanism of reaction of fluorides and pyrophosphates with barium titanate, the chemistry of which has hitherto received little consideration. The need for a many-sided approach to the investigation of the properties of $BaTiO_3$ has already been demonstrated [2, 3].

Melts of $BaTiO_3$ with fluorides and pyrophosphate of sodium or potassium are complex multicomponent systems (Na, Ba TiO_3, F, P_2O_7). Graphically such systems may be represented by prisms (Fig. 1). In this paper we submit the results of investigation by the visual-polythermic method of fusion to 1100° of the internal sections of these prisms; namely, the sections $Na_4F_4-Na_4P_2O_7-(BaTiO_3)_2$ and $K_4F_4-K_4P_2O_7-(BaTiO_3)_2$.

Starting substances. Polycrystalline $BaTiO_3$ was prepared by two fusions of chemically pure $BaCO_3$ with TiO_2 in stoichiometric ratios; the sodium and potassium fluorides were analytically pure grades with melting points of 982° (NaF) and 865° (KF). Sodium and potassium pyrophosphates were prepared by igniting chemically pure Na_2HPO_4 and K_2HPO_4. The melting points were 994°($Na_4P_2O_7$) and 1099° ($K_4P_2O_7$). All data are expressed in equimolar percentages.

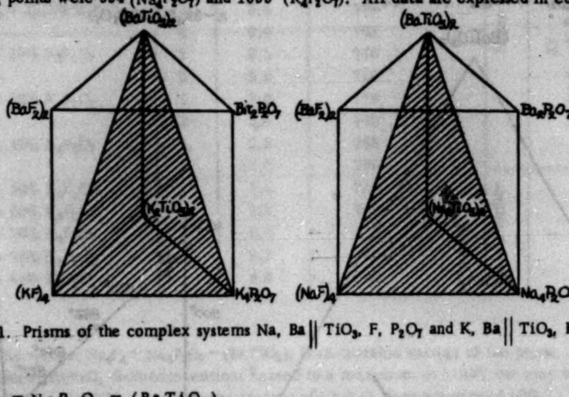

Fig. 1. Prisms of the complex systems Na, Ba $\|$ TiO_3, F, P_2O_7 and K, Ba $\|$ TiO_3, F, P_2O_7.

Section of $Na_4F_4-Na_4P_2O_7-(BaTiO_3)_2$

The sides $Na_4F_4-Na_4P_2O_7$ and $Na_4F_4-(BaTiO_3)_2$ (Figs. 2 and 3) are simple eutectic systems.

The side $Na_4P_2O_7-(BaTiO_3)_2$ (Fig. 2) is not a stable section of the reciprocal system $(BaTiO_3)_2 + Na_4P_2O_7 = Ba_2P_2O_7 + (Na_2TiO_3)_2$.

Optical examination of the phases crystallizing in the system in the range up to 1100° failed to reveal crystals of $BaTiO_3$. 10 internal cuts through the system $Na_4F_4-Na_4P_2O_7-(BaTiO_3)_2$ were investigated. Data for the cuts are set forth in Table 1.

The surface of crystallization of the section $Na_4F_4-Na_4P_2O_7-(BaTiO_3)_2$ up to 1100° is represented in Fig. 4. Fig. 5 is the projection of the lines of common crystallization of the system on the side $Na_4F_4-Na_4P_2O_7$.

It follows from the data obtained that the surface of crystallization of the section $Na_4F_4-Na_4P_2O_7-(BaTiO_3)_2$ up to a temperature of 1100° comprises four fields:

1) $Na_4P_2O_7$ and 2) NaF, occupying respectively 3.05 and 8.10% of the area of the system; 3) phases not established

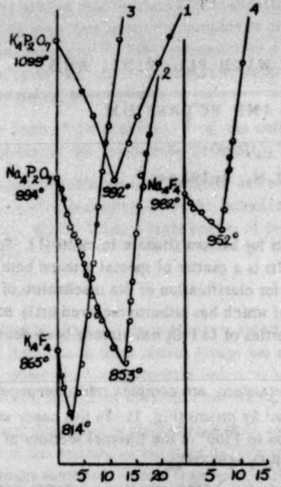

Fig. 2. Sides of sections through the complex systems. 1) $K_4P_2O_7 - (BaTiO_3)_2$, 2) $Na_4P_2O_7 - (BaTiO_3)_2$, 3) $K_4F_4 - (BaTiO_3)_2$, 4) $Na_4F_4 - (BaTiO_3)_2$.

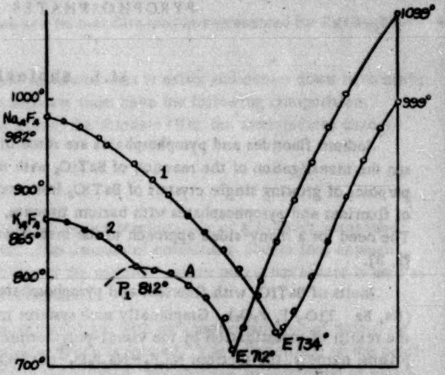

Fig. 3. Sides of sections through the complex systems. 1) $Na_4F_4 - Na_4P_2O_7$, 2) $K_4F_4 - K_4P_2O_7$. E) eutectic points; P_1—transition point; A $-3K_4F_4 \cdot K_4P_2O_7$.

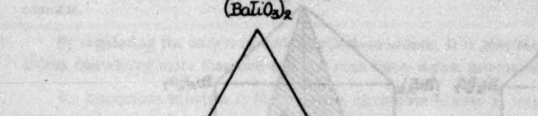
$(BaTiO_3)_2$
$BaTiO_3$
I
II
III
IV
V
VI
VII
VIII
IX
X
1000°
952°
852°
P
776°
714°
734°
Na_4F_4
982°
$Na_4P_2O_7$
999°

Fig. 4. Surface of crystallization of the section $Na_4F_4 - Na_4P_2O_7 - (BaTiO_3)_2$.
Explanation in text.

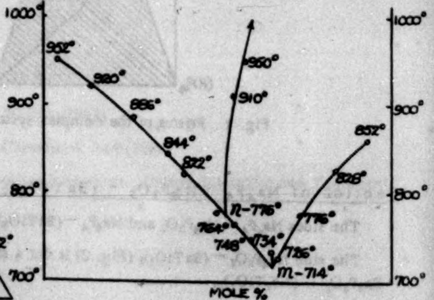

Fig. 5. Projection of lines of common crystallization on the side of sodium fluoride and pyrophosphate.
Explanation in text.

by us; and 4) $BaTiO_3$, occupying the greater part of the system. The system contains two quaternary, univariant points: point n corresponding to 48% $Na_4P_2O_7$, 8% $BaTiO_3$, 44% NaF and 776°, and point m, corresponding to 64% $Na_4P_2O_7$, 3.5% $BaTiO_3$, 32.5% NaF and 714°.

TABLE 1

Special points of the internal cuts

Cut Number	Composition of starting mixture of cuts in the direction of barium titanate	Points of intersection of branches of crystallization of the various phases		
		Point No.	BaTiO (mole-%)	Temperature
	To section $Na_4F_4 - Na_4P_2O_7 - Ba(TiO_3)_2$			
I	82.5% Na_4F_4 + 17.5% $Na_4P_2O_7$		5.5	920°
II	75% Na_4F_4 + 25% $Na_4P_2O_7$		5.0	886
III	65% Na_4F_4 + 35% $Na_4P_2O_7$		6.5	844
IV	60% Na_4F_4 + 40% NaP_2O_7		6.5	822
V	50% Na_4F_4 + 50% $Na_4P_2O_7$		8.0	776
VI	45% Na_4F_4 + 55% $Na_4P_2O_7$	1	4.5	764
		2	10.0	910
VII	40% Na_4F_4 + 60% $Na_4P_2O_7$	1	3.5	748
		2	12.5	950
VIII	32.5% Na_4F_4 + 67.5% $Na_4P_2O_7$		1.5	726
IX	25% Na_4F_4 + 75% $Na_4P_2O_7$		2.5	776
X	15% Na_4F_4 + 85 % $Na_4P_2O_7$		3.5	828
	To section $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$			
I	90% K_4F_4 + 10% $K_4P_2O_7$		4.5	798
II	80% K_4F_4 + 20% $K_4P_2O_7$		8.5	770
III	77.5% K_4F_4 + 22.5% $K_4P_2O_7$	1	5.5	776
		2	9.0	768
IV	74% K_4F_4 + 26% $K_4P_2O_7$	1	2.5	776
		2	9.0	790
V	70% K_4F_4 + 30% $K_4P_2O_7$	1	3.0	770
		2	9.5	832
VI	60% K_4F_4 + 40% $K_4P_2O_7$	1	2.5	753
		2	12.5	796
VII	50% K_4F_4 + 50% $K_4P_2O_7$		1.5	710
VIII	40% K_4F_4 + 60% $K_4P_2O_7$		1.5	745
IX	30% K_4F_4 + 70% $K_4P_2O_7$		2.0	804
X	25% K_4F_4 + 75% $K_4P_2O_7$		2.5	920
XI	15% K_4F_4 + 85% $K_4P_2O_7$		4.5	980

TABLE 2

Field Number	Name	Area occupied by each field as percentage of the total surface of the system
1	KF	2.13
2	$3K_4F_4 \cdot K_4P_2O_7$	1.74
3	$K_4P_2O_7$	4.37
4	Phase not accurately determined	Due to the high crystallization temperatures, the boundaries of the fields could not be completely delineated
5	$BaTiO_3$	Due to the high crystallization temperatures, the boundaries of the fields could not be completely delineated

Consequently, the system $Na_4F_4 - Na_4P_2O_7 - (BaTiO_3)_2$ is an unstable section of the prism. For the purpose of growth of single crystals of $BaTiO_3$ from compositions heated to a maximum of 1100°, use may be made of the compositions $[Na_4F_4 - Na_4P_2O_7] + (BaTiO_3)_2$, in which the amount of $Na_4P_2O_7$ does not exceed 50%.

Section $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$

Of the sides of the section, only the side of $K_4F_4 - (BaTiO_3)_2$ (Fig. 2) is a simple eutectic system. The side $K_4P_2O_7 - (BaTiO_3)_2$ (Fig. 2) evidently contains a product of exchange; it was optically established that the phase crystallizing at temperatures between 814 and 1100° is not barium titanate. In the system $K_4F_4 - K_4P_2O_7$ (Fig. 3) there is formed, in contrast to the corresponding sodium system, a compound $3K_4F_4 \cdot K_4P_2O_7$, melting with decomposition at 812°. An investigation was made of 11 internal cuts (see table). In Fig. 6 is represented the surface of crystallization up to 1100° of the system $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$. In Fig. 7 is shown the projection of the surface of crystallization of this system on to the $K_4F_4 - K_4P_2O_7$ side. We see that the surface of crystallization of the section $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$ comprises five fields (Table 2).

The greater part of the surface of the system is occupied by $BaTiO_3$.

In the section $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$ field 4 (evidently an exchange product) has penetrated deeply into the system. The system contains 3 univariant points; point m_1 at 19% $K_4P_2O_7$, 70.5% KF, 10.5% $BaTiO_3$ and 780°, n at 24% $K_4P_2O_7$, 73.5% KF, 2.5% $BaTiO_3$, 768°; and point m_2 at 54% $K_4P_2O_7$, 45% KF, 1.0% $BaTiO_3$ and 695°.

It should be noted that on cooling of compositions corresponding to cut II 80% K_4F_4 + 20% $K_3P_2O_7$ → $(BaTiO_3)_2$, the barium titanate crystallizes considerably more easily than on cooling of melts consisting only of a mixture of KF and $(BaTiO_3)_2$. On complete cooling of mixtures corresponding in composition to cut II, two layers are clearly formed, the upper one of which is $BaTiO_3$.

SUMMARY

1. A study was made up to 1100° by the visual-polythermic method of the surface of crystallization of the systems $Na_4F - Na_4P_2O_7 - (BaTiO_3)_2$ and $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$.

2. In the binary system $K_4F_4 - K_4P_2O_7$, in contrast to the corresponding system with participation of sodium salts, was found a compound $3K_4F_4 \cdot K_4P_2O_7$ which melts with decomposition and also appears conspiciously inside the section $K_4F_4 - (BaTiO_3)_2 - K_4P_2O_7$.

3. It was established that the systems $Na_4F_4 - Na_4P_2O_7 - (BaTiO_3)_2$ and $K_4F_4 - K_4P_2O_7 - (BaTiO_3)_2$ are unstable sections of the prisms Na, Ba || F, P_2O_7, TiO_3 and K, Ba || F, P_2O_7, TiO_3.

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* T.p. = C B. Translation pagination.

THE PREPARATION AND SOME PROPERTIES OF PHOSPHO-9-MOLYBDATES (LUTEOPHOSPHOMOLYBDATES) OF RUBIDIUM AND CESIUM

E.A. Nikitina and O.N. Sokolova

Some heteropoly acids give difficultly soluble rubidium and cesium salts and fairly highly soluble salts of potassium, sodium and magnesium. Investigation of the composition and solubility of these rubidium and cesium salts is of definite interest.

In the foreign literature [1] a method was published some while ago for quantitative determination of rubidium and cesium with the help of luteophosphomolybdic acid. Since we have worked out in detail [2] a method of preparation of this heteropoly acid, and since its potassium and sodium salts are soluble, it appeared expedient to make a critical evaluation of the proposed method.

The authors of the paper, O'Leary and Papish, described a method of preparation of luteophosphomolybdic acid $H_{12}[P_2O_2(Mo_2O_7)_9] \cdot x\,H_2O$, which consisted in heating commercial phosphomolybdic acid $H_7[P(Mo_2O_7)_6] \cdot xH_2O$ at 300-350° with continuous stirring until the yellow color had changed completely to green; the cooled acid was extracted with water; the reduced solution was oxidized with bromine water and slowly evaporated. Large yellow crystals came down which the authors assumed to be luteophosphomolybdic acid. They did not report an analysis of the crystals.

Precipitation of rubidium and cesium was effected with the help of luteophosphomolybdic acid prepared in the above fashion.

An attempt by the authors to establish the formula of the prepared cesium salt revealed that it is closer to the composition of the hexa-substituted salt than to the dodeca-substituted salt. As the authors admit, the analysis cannot be considered satisfactory since the composition of preparations obtained in presence of excess of one of the components differs from that of preparations isolated in presence of an excess of the other. Moreover, in both cases the sum of the components was less than 100% if reckoned on the MoO_3 and more if reckoned on the Mo_2O_7.

The cesium content of the prepared samples was 15 and 17%, calculated on the anhydrous composition. Instead of representing the composition of the salt by the appropriate formula on the basis of analysis of the prepared salt, the authors (ignoring the analytical data) assumed that they had obtained an actual salt of luteophosphomolybdic acid, and they attributed to it the formula $Cs_3PO_4 \cdot 9MoO_3$ (in the anhydrous form) or the same formula with 7 molecules of water in the hydrated form; the first of the proposed formulas corresponds to a cesium content of 22.3%; the second to 20.8%.

We see from the data submitted that the amount of cesium found does not correspond to the quantity of the latter in the trisubstituted salt of luteophosphomolybdic acid in question. The rubidium salt was not analyzed.

Our systematic study shows that the method of O'Leary and Papish cannot lead to luteophosphomolybdic acid without considerable contamination with the saturated heteropoly compound. Actually, on heating saturated phosphomolybdic acid to 300-350°, dehydration occurs as well as partial breakdown of the compound. The products of decomposition in this case are molybdic oxide and metaphosphoric acid.

During subsequent treatment with water, the remaining saturated phosphomolybdic acid naturally passes into solution together with the whole of the metaphosphoric acid which had been formed by breakdown of the complex, while the molybdenum oxide is precipitated.

The solution obtained after separation of the latter will contain free phosphoric acid. It was demonstrated that saturated phosphomolybdic acid in aqueous solution, in presence of phosphoric acid, partially changes into luteophosphomolybdic acid. This process took place also in the experiments of O'Leary and Papish who isolated a mixture of both acids and used it for determination of rubdium and cesium.

If O'Leary and Papish had made their observations on the basis of analytical results, they would have been convinced that the data obtained by them are in fairly good agreement with those calculated for the trisubstituted salt of saturated phosphomolybdic acid $Cs_3H_4[P(Mo_2O_7)_6] \cdot xH_2O$, which corresponds to a cesium content of 17.9% reckoned on the anhydrous composition of the salt. Evidently the cesium salt of saturated phosphomolybdic acid is less soluble than the analogous salt of lutephosphomolybdic acid, and if both acids were present in the solution with whose help the precipitation was effected, then a salt of saturated phosphomolybdic acid would be precipitated.

The authors of the cited paper overlooked these facts. Although unable, in the absence of analyses of the prepared salts, to prove the value of the proposed method of determination of rubidium and cesium, they nevertheless ventured to recommend luteo-phosphomolybdic acid as a reagent for quantitative determination of rubidium and cesium.

EXPERIMENTAL

For the purpose of proving the erroneousness of the proposed procedure, we synthesized the rubidium and cesium salts of luteo- and saturated phosphomolybdic acids and determined their solubility in water at 25°.

P_2O_5 was determined by the pyrophosphate method under the conditions described by Rakovsky and Nikitina [4]. Water was determined by igniting a weighed amount of the salt to constant weight after perliminary drying at 100°.

For determination of Rb_2O and Cs_2O, the solution of salts was precipitated with quinoline hydrochloride [5]; after removal of the heteropoly anion, the filtrate was evaporated to dryness and ignited to constant weight; from the weight of chlorides obtained the amount of Rb_2O and Cs_2O was calculated.

Using the published method [3], preparation was first carried out of saturated phosphomolybdic acid in which the water and P_2O_5 were determined. Results of the analysis are set forth in Table 1. The MoO_3 content was found by difference.

TABLE 1

Analysis of saturated phosphomolybdic acid

Component of acid	Found (in %)	Calculated on anhydrous composition (in %)	Calculation from formula $P_2O_5 \cdot 24MoO_3$ (in %)
H_2O	12.88	–	–
P_2O_5	3.42	3.93	3.95
MoO_3	83.70	96.07	96.05

Addition of the prepared acid to a dilute (1%) rubidium chloride solution produced a pale-yellow precipitate which was filtered, washed until there was a negative reaction for chlorine ion in the wash liquor, and dried in the air.

The cesium salt of saturated phosphomolybdic acid was prepared in a similar manner. Both preparations were analyzed for their content of water and P_2O_5; the P_2O_5 content based on the anhydrous composition was (in %): for the rubidium salt 3.22, for the cesium salt 3.14.

The P_2O_5 content of the rubidium salt of saturated phosphomolybdic acid, calculated from the formula $3Rb_2O \cdot P_2O_5 \cdot 24MoO_3$ is 3.41%; that of the analogous cesium salt is 3.2%. Consequently we had prepared the trisubstituted salts of saturated phosphomolybdic acid.

The solubility of both salts in water at 25° was studied. The solubility of the rubidium salt was 0.021, and that of the cesium salt was 0.013%, i.e. these salts of saturated phosphomolybdic acid are sparingly soluble in water.

In addition we synthesized the rubidium and cesium salts of luteophosphomolybdic acid. They were isolated in the form of pale-yellow solids by adding an excess of saturated solution of luteophosphomolybdic acid to a nearly saturated solution of rubidium or cesium chloride.

The prepared salts were pressed, washed with iced water until free from chlorine ion (test on wash liquors), and analyzed for their content of water, P_2O_5, Rb_2O and Cs_2O.

The MoO_3 content was found by difference.

The analytical results show that hexa-substituted salts of luteophosphomolybdic acid were obtained. The solubility of both salts in water at 25° was then determined. Withdrawal of samples for analysis of the liquid and solid phase was effected by the usually accepted methods. The content of Rb_2O and Cs_2O was determined in the solid phase; analysis confirmed that there was equilibrium between the liquid phase at the specified temperature and the same hexa-substituted rubidium and cesium salts of luteophosphomolybdic acid $Rb_6H_6[P_2O_2(Mo_2O_7)_9] \cdot xH_2O$ and $Cs_6H_6[P_2O_2(Mo_2O_7)_9] \cdot xH_2O$.

The results of the investigation are set forth in Table 3.

The determination of the solubility of the rubidium and cesium salts of luteo- and saturated phosphomolybdic acid in water at 25° showed that salts of saturated phosphomolybdic acid are slightly soluble; salts of luteophosphomolybdic acid are fairly soluble and cannot be used for analytical purposes; hence the results entirely refute the

TABLE 2

Analysis of cesium and rubidium salts of luteophosphomolybdic acid

Component of salt	Rubidium salt			Component of salt	Cesium salt		
	Found (in %).	Calculated on anhydrous comsition	Calculated on hexa-substituted salt		Found	Calculated on anhydrous comsition	Calculated on hexa-substituted salt
H_2O	11.13	–	–	H_2O	10.87	–	–
P_2O_5	3.90	4.39	4.31	P_2O_5	3.51	3.94	3.97
Rb_2O	15.24	17.15	17.02	Cs_2O	−21.14	23.72	23.62
MoO_3	69.73	78.46	78.67	MoO_3	−64.48	72.34	72.41

TABLE 3

Solubility of rubidium and cesium salts of luteophosphomolybdic acid in water at 25°

Salt of luteophosphomolybdic acid	Composition of liquid phase (grams of salt in 100 g solution)	Composition of crystal hydrate (in moles H_2O)
Rubidium	4.17	11.13
Cesium	5.08	10.87

recommended method of determination of rubidium and cesium. A suitable reagent for rubidium and cesium (in the absence of potassium) would be saturated phosphomolybdic acid since its rubidium and cesium salts are sparingly soluble.

SUMMARY

1. The hexa-substituted rubidium and cesium salts of luteophosphomolybdic acid were prepared.

2. The solubility in water of these salts at 25° was determined.

3. The solubility in water of the trisubstituted rubidium and cesium salts of saturated phosphomolybdic acid was determined; it was established that these salts are sparingly soluble.

4. It was shown that luteophosphomolybdic acid cannot be utilized as a reagent for quantitative determination of rubidium and cesium

5. Saturated phosphomolybdic acid can serve, in the absence of potassium, as a reagent for rubidium and cesium

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INVESTIGATION OF THE TERNARY RECIPROCAL SYSTEM OF THE ADIAGONAL-BELT TYPE COMPOSED OF THE SULFATES AND MOLYBDATES OF LITHIUM AND POTASSIUM

A.G. Bergman, A.I. Kislova and E.I. Korobka

The ternary reciprocal system of the sulfates and molybdates of lithium and potassium is a part of the surface of crystallization of the quaternary reciprocal system of the sulfates and molybdates of lithium, potassium and sodium which we have studied.

EXPERIMENTAL

The investigation was carried out by the visual-polythermal method. The temperature of crystallization of the melts was determined in a platinum crucible with a Pt-Pt, Rh thermocouple and a galvanometer with a scale reading to 17 mV. The accuracy of the determination was 1-2°. The melts were stirred with a platinum stirrer. The sulfates used were chemically pure grades, twice recrystallized. The molybdates were prepared from ammonium paramolybdate and the respective carbonates. Our data for melting points of the molybdates agreed with the literature data. All the salts were thoroughly dehydrated, prior to use.

The binary systems (Table 1 and 3, Fig. 1) $Li_2SO_4 - K_2SO_4$, $K_2MoO_4 - K_2SO_4$ and $Li_2MoO_4 - K_2MoO_4$, were previously investigated by Nacken and Amadori [1] and other authors. We repeated their determinations. Our results do not differ substantially from those of the earlier investigators. The system $Li_2MoO_4 - Li_2SO_4$, now studied by us for the first time, is a simple eutectic system.

A polymorphic transformation of lithium molybdate was detected at 630°. No clear indications of its existence appear in the literature [2]; in all cases, however, of investigation of both the binary systems and the cuts with participation of lithium molybdate, we clearly differentiated the change of phase at 630° accompanied by the appearance of a break on the curve.

The diagonal sections $Li_2MoO_4 - K_2SO_4$ and $Li_2SO_4 - K_2MoO_4$ (Tables 1 and 3, Fig. 2) pass through the field of the complex compound $Li_2SO_4 \cdot K_2SO_4$; hence they are not stable and do not participate in the triangulation of the system.

10 internal cuts were investigated in the reciprocal system (Tables 2 and 4, Figs. 3, 4 and 5). The presence was established of 8 fields of crystallization, the area of the square being apportioned as follows: fields of components – α-Li_2SO_4 2.44%, β-Li_2SO_4 3.80%, α-Li_2MoO_4 2.99%, β-Li_2MoO_4 18.46%, β-K_2SO_4 0.81%; fields of compounds – $Li_2SO_4 \cdot K_2SO_4$ 23.38%, $Li_2MoO_4 \cdot K_2MoO_4$ 6.77%; field of solid solutions $K_2[MoO_4, \alpha\text{-}SO_4]$ 43.35% (jointly with the fields of the components α-K_2SO_4 and K_2MoO_4 – products of decomposition of the solid solutions). The greater part of the area of the square is occupied by fields of complex compounds.

The transverse-belt cut IV (Fig. 4), composed of the complex compounds $Li_2SO_4 \cdot K_2SO_4$ and $Li_2MoO_4 \cdot K_2MoO_4$, located on opposite sides of the square of composition (Fig. 6), constitutes a simple eutectic system and divides the square of composition into two tetragons. The tetragons are subjected to a secondary triangulation by the sections extending from the vertices of the compounds to the vertex of the oppositely located component. The diagonals, however, as shown, do not participate in the triangulation; hence in the classification of Bergman and Bukhalova [3] the system belongs to the type of adiagonal-belt systems. Such systems occur in cases when the reaction of exchange decomposition between the components of the system gives way to the reaction of formation of complex compounds at two opposite sides of the square of composition, i. e., in our system we have

$$2Li_2MoO_4 + 2K_2SO_4 \rightarrow Li_2SO_4 \cdot K_2SO_4 + Li_2MoO_4 \cdot K_2MoO_4.$$

The system contains three eutectic points and one transition point (Table 5).

The invariant points and the lines of common crystallization of the components and their compounds have been projected on to the side of the $K_2MoO_4 - K_2SO_4$ square (Fig. 7). On the projection are also reflected the polymorphic transformations of the three components of the system: potassium sulfate at 596°, lithium sulfate at 574°, and lithium molybdate at 630° (straight lines).

TABLE 1

Sides and diagonal sections of the reciprocal system

Binary systems and diagonal sections	Starting component	Melting point of starting component	Component added	Crystallization branches and their points of intersection			
				Branch 1	Intersection of 1 and 2		Branch 2
					A*	B**	
$Li_2MoO_4 - K_2MoO_4$	Li_2MoO_4	705	K_2MoO_4	α-Li_2MoO_4	14.5	630	β-Li_2MoO_4
$Li_2MoO_4 - Li_2SO_4$	Li_2MoO_4	705	Li_2SO_4	α-Li_2MoO_4	35.5	630	β-Li_2MoO_4
$K_2MoO_4 - K_2SO_4$	K_2MoO_4	924	K_2SO_4	$K_2[MoO_4, \alpha$-$SO_4]$	—	—	—
$Li_2SO_4 - K_2SO_4$	Li_2SO_4	858	K_2SO_4	α-Li_2SO_4	12.5	574	β-Li_2SO_4
$Li_2MoO_4 - K_2SO_4$	Li_2MoO_4	705	K_2SO_4	α-Li_2MoO_4	11.5	630	β-Li_2MoO_4
$Li_2SO_4 - K_2MoO_4$	Li_2SO_4	858	K_2MoO_4	α-Li_2SO_4	10	574	β-Li_2SO_4

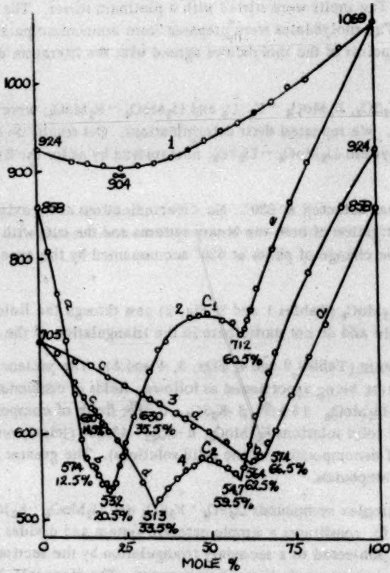

Fig. 1. Sides of the square of the reciprocal system.
1) $K_2MoO_4 - K_2SO_4$, 2) K_2SO_4, 3) $Li_2MoO_4 - Li_2SO_4$,
4) $Li_2MoO_4 - K_2MoO_4$;
a) α-Li_2SO_4, b) β-Li_2SO_4, c) α-Li_2MoO_4,
d) β-Li_2MoO_4, e) α-K_2SO_4;
C_1 – $Li_2SO_4 \cdot K_2SO_4$, C_2 – $Li_2MoO_4 \cdot K_2MoO_4$.

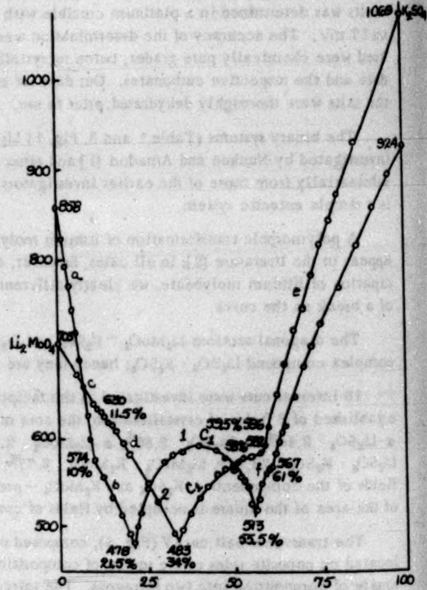

Fig. 2. Diagonal sections.
1) $Li_2SO_4 - K_2MoO_4$, 2) $Li_2MoO_4 - K_2SO_4$;
a) α-Li_2SO_4, b) β-Li_2SO_4, c) α-Li_2MoO_4,
d) β-Li_2MoO_4, e) α-K_2SO_4, f) β-K_2SO_4;
C_1 – $Li_2SO_4 \cdot K_2SO_4$.

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* Per cent of binary component

** Temperature

Table 1 continued

Crystallization branches and their points of intersection										Melting point			Fig. No.
Intersection of 2 and 3		Branch 3	Intersection of 3 and 4		Branch 4	Intersection of 4 and 5		Branch 5	of added component	of compound	eutectic	
A	B		A	B		A	B					
33.5	513	$Li_2MoO_4 \cdot K_2MoO_4$	59.5	547	K_2MoO_4	–	–	–	924	569	513, 547	1
62.5	564	β-Li_2SO_4	66.5	574	α-Li_2SO_4	–	–	–	858	–	564	
–	–	–	–	–	–	–	–	–	1069	–	–	
20.5	532	$Li_2SO_4 \cdot K_2SO_4$	60.5	712	α-K_2SO_4	–	–	–	1069	736	532, 712	
34	483	$Li_2SO_4 \cdot K_2SO_4$	58	582	β-K_2SO_4	59.5	596	α-K_2SO_4	1069	–	–	2
21.5	478	$Li_2SO_4 \cdot K_2SO_4$	55.5	513	β-K_2SO_4	61	567	K_2MoO_4	924	–	–	

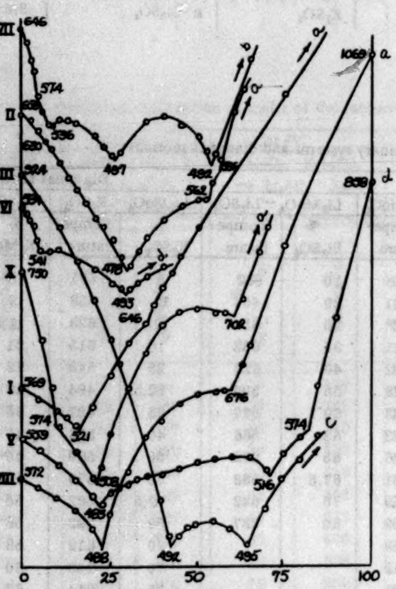

Fig. 3. Internal cuts in the directions: → a – K_2SO_4, → b – K_2MoO_4, → c – Li_2MoO_4 → → d – Li_2SO_4.

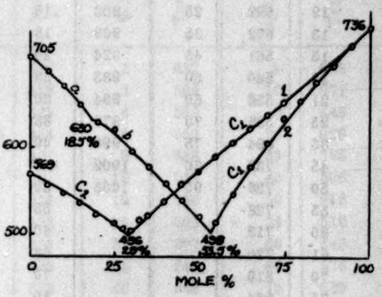

Fig. 4. Stable internal cuts. 1) IV, 2) IX. a) α-Li_2MoO_4, b) β-Li_2MoO_4; C_1 – $Li_2SO_4 \cdot K_2SO_4$, C_2 – $Li_2MoO_4 \cdot K_2MoO_4$.

TABLE 2

Internal cuts of the reciprocal system

Cut Number	Starting mixture of components (in %)	Melting point of starting mixture	Component added	Crystallization branches and their intersection points		
				Branch 1	Intersection of 1 and 2	
					A *	B**
I	$50\%K_2MoO_4 + 50\%Li_2MoO_4$	569	K_2SO_4	$Li_2MoO_4 \cdot K_2MoO_4$	16.5	521
II	$90\%Li_2MoO_4 + 10\% K_2MoO_4$	658	K_2SO_4	α-Li_2MoO_4	4.5	630
III	$45\%K_2SO_4 + 55\ K_2MoO_4$	924	Li_2MoO_4	$K_2[MoO_4, \alpha$-$SO_4]$	43	492
IV	$50\% Li_2MoO_4 + 50\%K_2MoO_4$	569	$Li_2SO_4 \cdot K_2SO_4$	$Li_2MoO_4 \cdot K_2MoO_4$	29	496
V	$45\%K_2MoO_4 + 55\%Li_2MoO_4$	559	Li_2SO_4	$Li_2MoO_4 \cdot K_2MoO_4$	22	483
VI	$62.5K_2MoO_4 + 37.5Li_2MoO_4$	594	Li_2SO_4	$K_2[MoO_4, \alpha$-$SO_4]$	5.5	541
VII	$25\%Li_2MoO_4 + 75\%Li_2SO_4$	646	K_2MoO_4	α-Li_2SO_4	3.5	574
VIII	$40\%Li_2MoO_4 + 60\%Li_2SO_4$	572	K_2SO_4	α-Li_2MoO_4	23	488
IX	$50\%Li_2SO_4 + 50\%K_2SO_4$	736	Li_2MoO_4	$Li_2SO_4 \cdot K_2SO_4$	53.5	498
X	$12.5Li_2MoO_4 + 87.5Li_2SO_4$	750	K_2SO_4	α-Li_2SO_4	8.5	574

TABLE 3

Temperature of start of crystallization of melts of binary systems and diagonal sections*

Binary systems								Diagonal sections			
$Li_2SO_4 - K_2SO_4$		$K_2MoO_4 - K_2SO_4$		$Li_2MoO_4 - K_2MoO_4$		$Li_2MoO_4 - Li_2SO_4$		$Li_2MoO_4 - K_2SO_4$		$Li_2SO_4 - K_2MoO_4$	
% K_2SO_4	Temperature	% K_2SO_4	Temperature	% K_2MoO_4	Temperature	% Li_2SO_4	Temperature	% K_2SO_4	Temperature	% K_2MoO_4	Temperature
5	760	10	912	10	658	10	682	5	671	5	718
10	645	20	906	12.5	641	20	664	10	638	9	598
12	592	25	903	15	628	25	654	12	628	12.5	556
13	572	35	909	18	611	35	632	15	615	21	484
15	561	45	924	20	602	40	622	25	549	22	500
19	540	50	933	25	578	50	599	32.5	494	25	542
21	536	60	954	30	543	60	572	35	497	35	585
25	588	70	978	35	523	63	566	40	533	40	591
35	694	75	993	40	546	65	572	50	569	45	585
45	732	80	1002	45	561	67.5	588	55	579	50	565
50	736	90	1038	50	569	75	642	57.5	582	55	526
55	728			55	559	80	687	59	592	56	519
60	713			60	559			60	612	58	549
61	720			64	619			70	743	60	565
70	810			70	691			75	814	62	582
75	864			80	783			85	924	75	727
80	908			90	859					90	855

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* The number of experimental points is considerably reduced (Figs. 1 and 2).

** In the table are included the most important cuts. The number of points is cut down (Figs. 3 and 4).

Table 2 continued

Crystallization branches and their points of intersection										Fig. No.
Branch 2	Intersection of 2 and 3		Branch 3	Intersection of 3 and 4		Branch 4	Intersection of 4 and 5		Branch 5	
	A	B		A	B		A	B		
K_2MoO_4	35.5	646	K_2SO_4	–	–	–	–	–	–	3
α-Li_2MoO_4	29	478	$Li_2MoO_4 \cdot K_2MoO_4$	53	562	β-K_2SO_4	55.5	596	α-K_2SO_4	3
$Li_2MoO_4 \cdot K_2MoO_4$	65.5	495	β-Li_2MoO_4	–	–	–	–	–	–	3
$Li_2SO_4 \cdot K_2SO_4$	–	–	–	–	–	–	–	–	–	4
β-Li_2MoO_4	71.5	516	β-Li_2SO_4	83	574	α-Li_2SO_4	–	–	–	3
$Li_2MoO_4 \cdot K_2MoO_4$	29	493	$Li_2SO_4 \cdot K_2SO_4$	–	–	–	–	–	–	3
β-Li_2SO_4	7	536	β-Li_2MoO_4	26	497	$LiSO_4 \cdot K_2SO_4$	53.5	492	$K_2[MoO_4, \alpha$-$SO_4]$	3
$Li_2SO_4 \cdot K_2SO_4$	60	676	$K_2[MoO_4, \alpha$-$SO_4]$	–	–					3
β-Li_2MoO_4	18.5	630	α-Li_2MoO_4	–	–			–		4
β-Li_2SO_4	21	508	$Li_2SO_4 \cdot K_2SO_4$	60.5	702	$K_2[MoO_4, \alpha$-$SO_4]$	–	–		3

TABLE 4

Temperature of start of crystallization of melts of the internal cuts *

Cut I		Cut III		Cut IV		Cut V		Cut VII		Cut IX	
50% Li_2MoO_4 50% K_2MoO_4 → K_2SO_4		45% K_2SO_4 55% K_2MoO_4 → Li_2MoO_4		$Li_2MoO_4 \cdot K_2MoO_4$ → $Li_2SO_4 \cdot K_2SO_4$		45% K_2MoO_4 55% Li_2MoO_4 → Li_2SO_4		25% Li_2MoO_4 75% Li_2SO_4 → K_2MoO_4		Li_2MoO_4 → → $Li_2SO_4 \cdot K_2SO_4$	
% K_2SO_4	Temperature	% Li_2MoO_4	Temperature	% $Li_2SO_4 \cdot K_2SO_4$	Temperature	% Li_2SO_4	Temperature	% K_2MoO_4	Temperature	% $Li_2SO_4 \cdot K_2SO_4$	Temperature
5	556	10	864	10	546	5	546	1	632	5	688
10	543	20	780	15	536	10	529	3	599	10	671
15	526	25	737	25	510	20	493	4	569	15	649
20	549	35	622	30	500	22.5	484	5	553	20	629
25	585	40	549	35	519	25	497	8	536	30	595
30	622	42.5	507	45	556	30	507	10	543	40	556
35	645	45	507	50	572	35	516	15	540	50	516
37.5	668	50	520	60	605	45	526	25	503	55	510
42.5	705	55	523	70	638	55	536	27.5	507	60	543
50	756	60	516	75	652	65	539	35	543	65	576
75	914	65	497			70	523	40	549	75	632
		70	540			75	543	50	526	85	674
		80	599			80	562	52.5	510		
		85	625			85	623	55	507		
								65	616		

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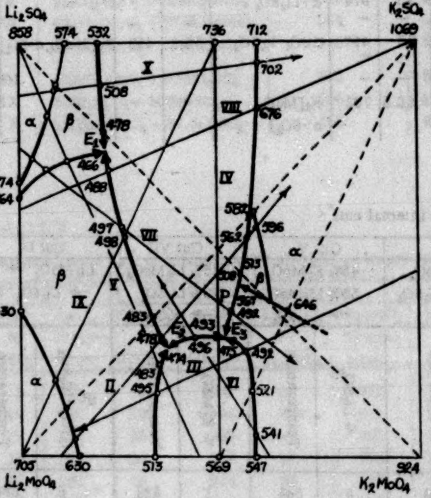
* In the table are included the most important cuts. The number of points is cut down (Figs. 3 and 4).

TABLE 5

Compositions and temperatures of the invariant points

Designations of points	Character of points	Temperature	Composition (in mole-%)				Equilibrium phases
			Li_2MoO_4	K_2SO_4	K_2MoO_4	Li_2SO_4	
E_1	Eutectic	466	25.5	22.0	–	52.5	β-Li_2So_4, $Li_2SO_4 \cdot K_2SO_4$, β-Li_2MoO_4
E_2		474	36.5	–	37.5	26.0	β-Li_2MoO_4, $Li_2SO_4 \cdot K_2SO_4$, $Li_2MoO_4 \cdot K_2MoO_4$
E_3		475	48.5	29.0	22.5	–	K_2MoO_4, $Li_2SO_4 \cdot K_2SO_4$, $Li_2MoO_4 \cdot K_2MoO_4$
P	Transition	508	44.5	42.0	13.5	–	$Li_2SO_4 \cdot K_2SO_4$, K_2MoO_4, β-K_2SO_4



Li_2SO_4
858
574
532
736
712
K_2SO_4
1069
702
X
508
VIII
676
α
β
478
E_1
466
488
IV
574
564
497
498
VII
582
596
562
α
515
509
β
P
567
β
IX
V
493
E_3
646
630
483
E_2
478
474
436
475
492
III
483
495
VI
521
α
II
541
705
630
513
569
547
924
Li_2MoO_4
K_2MoO_4

Fig. 5. Direction of internal cuts.

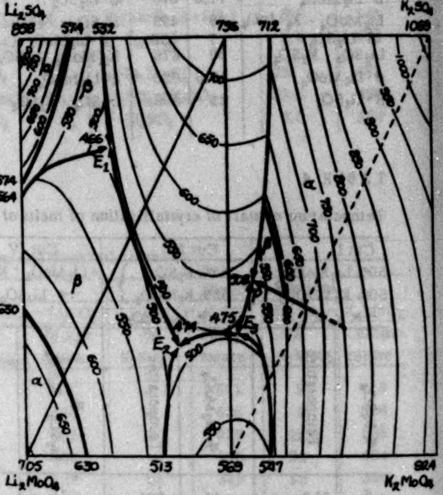


Fig. 6. Projection of the diagram of the reciprocal system on to the square of composition.

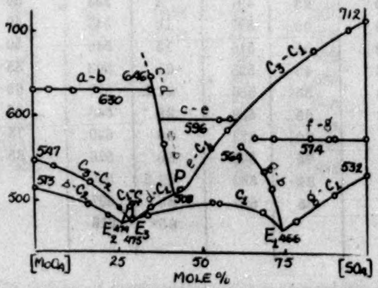


Fig. 7. Projection of the crystallization tree on to the $K_2MoO_4 - K_2SO_4$ side.
a) a-Li_2MoO_4, b) β-Li_2MoO_4, c) α-K_2SO_4, d) K_2MoO_4, e) β-K_2SO_4, f) Li_2SO_4, g) β-Li_2SO_4;
C_1 – Li_2SO_4 K_2SO_4, C_2 – $Li_2MoO_4 \cdot K_2MoO_4$, C_3 – – $K_2[MoO_4, \alpha\text{-}SO_4]$.

SUMMARY

1. The surface of crystallization of the ternary reciprocal system of the sulfates and molybdates of lithium and potassium was investigated by the visual-polythermal method.

2. For the first time a study was made of the binary system $Li_2MoO_4 - Li_2SO_4$, which constitutes a simple eutectic system with a eutectic point at 564° and 62.5% Li_2SO_4.

3. A special feature of the system is the formation of complex compounds at two opposite sides of the square: $Li_2SO_4 - K_2SO_4$ and $Li_2MoO_4 \cdot K_2MoO_4$. The transverse, so-called "belt", section constituted by these complex compounds forms a simple eutectic system and is stable; it divides the square of composition into two tetragons. Further triangulation of the tetragons into simplex figures is effected by sections constituted by complex compounds and the oppositely

situated components. One of them, $Li_2SO_4 \cdot K_2SO_4 - Li_2MoO_4$, is stable. On the basis of the foregoing observations, the system belongs to the eutectic type of adiagonal-belt systems. Consequently the reaction of formation of complexes distributed over two opposing sides of the square predominates over the reaction of exchange decomposition.

The diagonal sections are not stable and do not participate in the triangulation of the system.

4. The solid solutions formed on the side of the square of compositions between the components α-K_2SO_4 and K_2MoO_4 also extend inside the system, but with increasing content of the third component they become unstable and break down.

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* T. p. = C. B. Translation pagination.

EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM CONSTANT OF THE REACTION OF DECOMPOSITION OF MAGNESIUM HYDROXIDE

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In the literature on the decomposition of magnesium hydroxide and its thermodynamic characteristics there are no direct experimental data on the determination of the equilibrium constant of this reaction. The temperature dependence of the equilibrium constant is unknown; also, there is some discrepancy between the existing values of the thermal effect of the reaction. For example, according to the data of Fricke and Lüke [1] the heat of formation (Q_0) of magnesia from the hydroxide, determined calorimetrically from indirect data, ranges from 18.62 to 21.34 kcal; according to Johnston [2] the value is 13.10 kcal; according to Mixter [3] it is 9.4 kcal.

Thermochemical calculation on the basis of Hess' law, using existing tables of data [4, 5] ($\Delta H^0_{Mg(OH)_2}$ = = 218.7 kcal, ΔH^0_{MgO} = 146.1 kcal and $\Delta H^0_{H_2O}$ = 57.8 kcal.),* gives a value of 14.8 kcal.

In view of the contradictory character of existing literature data, it was of interest to undertake a direct experimental investigation of the equilibrium constant of the reaction of dehydration of magnesium hydroxide over a wide temperature range.

Dehydration of magnesium hydroxide is an endothermic process proceeding with separation of one product in the gas (vapor) phase: $Mg(OH)_2 = MgO + H_2O$ (gas).

Consequently the magnitude of the equilibrium constant in this case is governed by the equilibrium value of the fugacity of water vapor over a mixture of solid magnesia and magnesium hydroxide.

The apparatus selected for measurement of the equilibrium fugacity of the vapor consisted of a high-pressure bomb (volume 135 ml) placed in an electric furnace, and a pressure gage.

The set-up is illustrated in Fig. 1. In order to avoid condensation of water vapor in the inner chamber (Bourdon chamber) of the pressure gage, the latter was filled with water. The narrow connecting tube between the gage and the head of the bomb was likewise filled with water. A platinum-platinorhodium thermocouple was fixed to the body of the bomb for measurement of temperature. Magnesium hydroxide was prepared by treating magnesium sulfate with caustic alkali and washing the precipitate free from sulfate ions before drying to constant weight in a thermostat at 150°. The water content of the magnesium hydroxide was 30.9%, i.e., the theoretical amount. The experimental procedure was as follows. Small tablets of the prepared magnesium hydroxide were carefully screened to remove powdery hydroxide, which could choke the connecting tube (during measurements), and placed in the bomb. The amount charged into the bomb was 120 ml (about 60 g).

Before the start of the measurements, the whole apparatus was tested for tightness; then the electric furnace was switched on, and with the help of a transformer the necessary temperature was established; then the measurements were performed.

As special experiments at 450° showed, equilibrium pressure was established after 3 hours; at 500-650° it was established in 1.5-2 hours. The magnitudes of the equilibrium pressure at various temperaturea are shown in the table.

The dependence of the equilibrium pressure on the temperature is plotted in Fig. 2.

Utilizing the isochoric equation

$$\frac{d \ln K_V}{dT} = \frac{-Q_V}{RT^2} \tag{1}$$

where K_V – is the equilibrium constant at constant volume; Q is the thermal effect of the reaction at constant volume we can determine the thermal effect of the reaction.

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* ΔH^0 – is the change of heat content accompanying the reaction of formation of 1 mole of a given substance from the elements in their standard state.

Values of equilibrium pressure of water vapor in the decomposition of magnesium hydroxide at various temperatures

Temperature	Pressure ($P_{atm.}$)
380°	34
430	64
475	100
516	140
550	200
600	298
650	420

For this purpose Equation (1) was taken in the integrated form:

$$\ln K_v = \ln P_{equil.} = \frac{Q_v}{RT} + B \qquad (2)$$

As we see from Fig. 3, the dependence of the logarithm of the equilibrium pressure on the reciprocal of the temperature is well expressed by a straight line, indicating substantial constancy of Q_v over the range of temperatures studied.

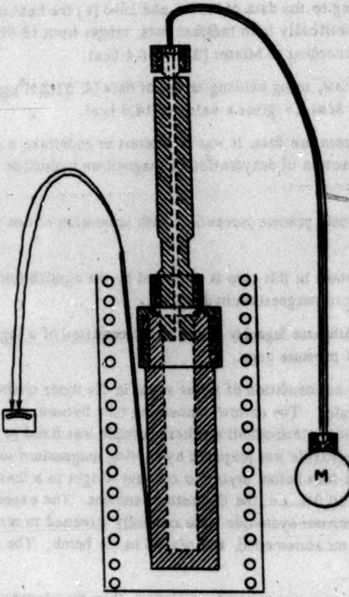

Fig. 1. Diagram of apparatus for determination of equilibrium pressure of water vapor

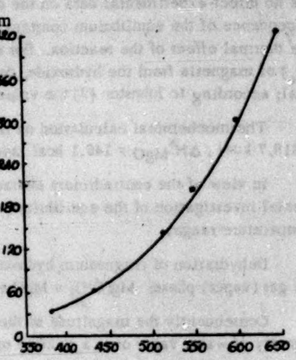

Fig. 2. Dependence of equilibrium pressure of water vapor during decomposition of magnesium hydroxide on the temperature.

The magnitude of the thermal effect, calculated from the tangent of the angle of slope of the straight line, is 11,000 cal/mole, while B is 5.24. Equation (2) thus acquires the form:

$$\log K_V = \log P_{equil.} = \frac{11000}{4.575T} + 5.24. \qquad (3)$$

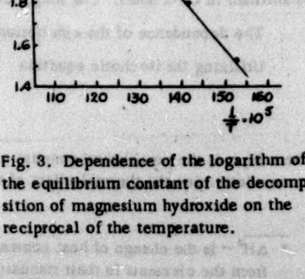

Fig. 3. Dependence of the logarithm of the equilibrium constant of the decomposition of magnesium hydroxide on the reciprocal of the temperature.

SUMMARY

1. The equilibrium pressure and equilibrium constant of the decomposition of magnesium hydroxide in the temperature range of 380-650° were determined.

2. On the basis of experimental data and using the

isochore equation, a value of 11,000 cal/mole was found for the thermal effect of the reaction.

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HETEROTRIACIDS

III. SILICOTUNGSTOVANADIC ACID

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Due to the formation in an acidic medium of the sparingly soluble tungstic acid, the synthesis of heteropoly acids containing tungsten proceeds with considerably greater difficulty than the preparation of analogous compounds of molybdenum.

This difficulty is eliminated by a number of authors [1] in the preparation of silicotungstic acid by preliminary conversion of the tungstate used for the synthesis into an acid-soluble paratungstate by careful neutralization with strong acids of the hot solution of the normal tungstate. The resultant reaction proceeds according to the equation:

$$12Na_2WO_4 + 14HCl = 5Na_2O \cdot 12WO_3 + 14NaCl + 7H_2O.$$

It was quite natural to use this preparative method for the synthesis of silicotungstovanadic acid. Starting from the previously prepared sodium paratungstate, silicate and metavanadate, Gritskaya carried out a large number of experiments on the preparation of the heterotriacid by the etherate method, and a large number of factors bearing upon the process of separation of the compound concerned in the free state were investigated. With various ratios of starting substances in a weakly acid medium, with boiling, the solution in all cases had a yellow color. This distinguished it, above all, from the solutions that we obtained under similar conditions during preparation of all other heterotriacids containing vanadium, the color of which was bright-red.

In preparing the etherate from this yellow solution, a precipitate began to form even at an acidity of 0.8 N hydrochloric acid, and the size of the precipitate increased on supplementary addition of acid. In some experiments a small amount of colorless etherate was obtained, evidently silicotungstic acid. The $V_2O_6^{--}$ radical did not enter the complex ion. We also failed to obtain silicotungstovanadic acid by reaction under various conditions of excess of vanadate with prepared silicotungstic acid. However, a simple change in the procedure for the preparation, namely, neutralization of normal sodium tungstate with hydrochloric acid in presence of silicate (two-fold excess) under otherwise identical conditions, led to formation of a silicotungstovanadic complex which gave an etherate. On shaking this solution with ether in a hydrochloric acid medium (4 N) there was formed a relatively small quantity of yellow etherate from which, after its decomposition, could be isolated crystals of yellow color. Judging by the color of the crystals, vanadium was present in the form of the VO_3^{--} radical. Analysis showed that vanadium was present in extremely small amount, the ratio of V to W being 1:34. It is perfectly obvious that the introduction of vanadium under these conditions is only effected with great difficulty.

We carried out further investigations on the determination of the most favorable conditions for maximum introduction of vanadium into the complex ion of silicotungstovanadic acid of the saturated type. We were able to establish that the synthesis is successful if we start not from paratungstate but from a product containing anions of metatungstic acid.

Formation of anions of metatungstic acid from normal tungstate proceeds according to the equation:

$$WO_4^{--} + 3WO_3 = W_4O_{13}^{--}$$

On the basis of the equation, each gram of $Na_2WO_4 \cdot 2N_2O$ requires 2.3 g H_2WO_4. In our experiments we gradually added to a boiling solution of normal sodium tungstate, with constant stirring, powdered tungstic acid until a small amount of acid remained unreacted under these conditions. The amount of the latter introduced was 1 g per gram of sodium tungstate, i.e., the above reaction did not proceed to completion. After filtration, addition was made to the resultant mixture, heated to boiling in a conical flask, of a hot mixture of solutions of sodium metavanadate ($NaVO_3$) and soidum silicate ($Na_2SiO_3 \cdot 9H_2O$). The solution in the flask immediately turned an orange color. The contents of the flask were boiled with periodical addition of water so that the volume of liquid remained unchanged. A study of the influence of the duration of boiling on the course of synthesis showed that silicotungstovanadic acid may be formed after only 5-10 minutes' boiling, but in that case the yield of etherate is considerably reduced because formation of the latter is accompanied by precipitation of tungstic acid, which contaminates the etherate. Good results are obtained by boiling for 1 $^1/_2$ hours.

After boiling for the specified period, dropwise addition is made (without lifting the flask from the hot plate) of sufficient H_2SO_4 (1:1) to impart an acidity of 10-12 N H_2SO_4. The contents of the flask are then cooled under the tap and transferred to a separating funnel; ether is added and the mixture shaken. The resultant drops of orange-colored etherate fall to the bottom of the funnel. More complete separation of etherate can be achieved if toward the end of the shaking a further small amount of H_2SO_4 (1:1) is introduced. The separated etherate is washed with 10 N H_2SO_4 saturated with ether, and after thorough cooling it is placed in a shallow crystallizing dish. The etherate is decomposed by addition of water until "boiling-up" ceases. The residual ether is driven off by careful heating in water at 60-70°. On standing for about 24 hours, orange crystals of silicotungstovanadic acid are formed and are separated from mother liquor by filtration through a funnel with a porous base before drying on a watch glass at room temperature.

In some of our preparative experiments we took the following amounts of starting substances: $N_2SO_4 \cdot 2H_2O$ – 16.5 g; $NaVO_3$ – 5.8 g; and $Na_2SiO_3 \cdot 9H_2O$ – 2.8 g. These amounts were calculated from the ratio Si : W : V = = 1 : 10 : 4, i.e. the amount of vanadate was twice as large as is required by the formula $H_8[Si(W_2O_7)_5V_2O_6]$. The optimum volume of solution in which the complex was prepared by boiling was 50-60 ml. At higher dilutions the yield of etherate decreases. Prior to the boiling, 2 ml H_2SO_4 (1 :1) was added, and after 1 $^1/_2$ hours 75 ml was added. The yield of product was 70% of the theoretical.

Analysis. The water of crystallization in the synthesized compound was determined by drying and by the hydride method.

Silicon was determined from the loss in weight of the sum of the oxides after working up with hydrofluoric acid under the previously described conditions [2].

For determination of vanadium and tungsten, a weighed amount of the heterotriacid of the order of 0.7-g was dissolved in a 100 ml measuring flask.

The vanadium was determined in 10 ml of the prepared solution after decomposing the silicotungstovanadic complex with 25 ml of a mixture of equal volumes of H_2SO_4 (d 1.84), H_3PO_4 (d 1.7) and water. Heating was carried out until the solution had acquired a blue color. Water was then added to make up the volume to 50 ml and titration was performed with Mohr's salt in presence of phenylanthranilic acid until the blue-violet color disappeared.

In another aliquot portion (10 ml) of the solution was determined the sum of tungsten and vanadium. This was done by transferring the solution to a funnel of 200 ml capacity fitted with a bottom ground-glass tap and a side tap (also ground-glass) situated one-third of the way down from the stopper. The side tube was connected to a 10 ml receiver filled with freshly boiled water saturated with carbon dioxide. Into the funnel was introduced 10 ml lead amalgam and 40 ml HCl (d 1.19); it was then heated in a beaker containing hot water (80-90°), the funnel being arranged with the open stopper on its side so that it was supported by the walls of the beaker. Heating was carried out for 5-10 minutes, and then carbon dioxide was passed in through the side tap from a Kipp's apparatus (with half-opened tap) and the funnel was vigorously shaken (10-15 minutes) until the solution had a khaki color. After reduction of the tungsten to the trivalent and vanadium to the pentavalent form, the amalgam was transferred to the receiver, and the solution into a twofold excess of standard 0.05 N potassium bichromate solution, the lead from the Kipp's apparatus having been connected to the side tap of the funnel and the lower tap of the funnel to a glass tube extending to the bottom of the vessel containing the bichromate solution. In this way the vanadium was oxidized to the tetravalent form and the tungsten to the hexavalent form which was precipitated as tungstic acid. The excess of bichromate was titrated with thiosulfate solution in presence of 0.2 g potassium iodide and starch until appearance of a grey-green color (with a yellow tinge).

Knowing the total of tungsten and vanadium and the amount of vanadium separately, the tungsten could be calculated by difference.

In the following table are set forth the results of analysis of three specimens of synthesized heterotriacid. For the sake of brevity we only give the weights taken for determination of the silica content; the content of the other components and of water of crystallization was calculated from these weights.

Products obtained by utilizing paratungstate and metatungstate as starting substances are readily soluble in water, and in presence of inorganic acids they do not form a precipitate of tungstic acid.

Treatment with 5% solution of o-hydroxyquinoline in acetic acid brings down yellow precipitates even at an acidity reaching 1.3 N HCl, whereas, from the separately taken sodium vanadate and sodium tungstate, vanadium comes down at an acidity not exceeding 0.001 N and tungsten at an acidity not exceeding 10^{-5} N. Analysis of the precipitates obtained in a hydrochloric acid medium showed that the ratios of $SiO_2:WO_3:V_2O_5$ scarcely differed from the ratios found for aqueous solutions of the heterotriacids in question, as seen from Table 2 in which are set forth the mean values of the three analyses.

TABLE 1

Results of analysis of silicotungstovanadic acid

Specimen Number	Weight (in g)	SiO_2		WO_3		V_2O_5		H_2O		Ratio
		(g)	(mole)	(g)	(mole)	(g)	(mole)	(g)	(mole)	$SiO_2 : WO_3 : V_2O_5 : H_2O$
1	0.779	0.0135	0.00022	0.550	0.00237	0.041	0.00022	0.102	0.00566	1 : 10.8 : 1 : 26
2	0.771	0.012	0.00022	0.498	0.00215	0.042	0.00023	0.140	0.00777	1 : 9.8 : 1.1 : 35
3	0.854	0.015	0.00024	0.548	0.00237	0.056	0.00031	0.159	0.00883	1 : 9.9 : 1.3 : 37

TABLE 2

Heterotriacid	Analysis of solution	Analysis of precipitate from o-hydroxyquinoline
	$SiO_2 : WO_3 : V_2O_5$	$SiO_2 : WO_3 : V_2O_5$
Prepared from paratungstate	1 : 34 : 0.5	1 : 3.6 : 0.5
Prepared from metatungstate	1 : 10.2 : 1	1 : 10.1 : 0.98

EVALUATION OF RESULTS

All our studies of the synthesis of silicotungstovanadic acid showed that the decisive factor in the formation of the heteroion of the given compound is the nature of the tungstate anion used as starting substance. During formation of silicotungstic acid, the transition of normal tungstate into paratungstate is not accompanied by formation of precipitated tungstic acid in the process of formation of the etherate, whereas this effect does not arise in the present case. The silicotungstovanadic acid separated by employing paratungstate differs sharply from other vanadic heterotriacids synthesized by us by virtue of its color and its very low content of vanadium; evidently it belongs to another series of compounds. The tendency to crystallize and the precipitating action of o-hydroxyquinoline indicate that it is an individual substance.

An entirely different result is obtained on synthesis after preliminary conversion of tungstate into metatungstate. Tungstic acid is then not precipitated during formation of the etherate. Introduction of vanadium proceeds without special difficulties. The resultant compound is bright-red, justifying the conclusion that the $V_2O_6^{--}$ radical was introduced. Analyses of three samples of synthesized products show that they are all heterotriacids of the saturated type – $H_8[Si(W_2O_7)_5V_2O_6] \cdot nH_2O$. Slight deviations in the ratio of $WO_3 : V_2O_5 = 10 : 1$ are clearly explained by the difficulty of accurate determination of small amounts of vanadium in presence of a large content of tungsten.

The great difference between the crystal water content of the first specimen on the one hand and the second and third specimens on the other is accounted for by the conditions of crystallization; observations show that the slower the crystallization the higher the crystal water content of the hydrates.

SUMMARY

1. Conditions were established for the synthesis by the etherate method, and silicotungstovanadic acid was isolated in the crystalline form.

2. It is shown that the decisive factor for synthesis of this acid is previous conversion of normal tungstate into metatungstate.

3. Determination of the composition of the heterotriacid indicated that it may be represented by the formula $H_8[Si(W_2O_7)_5V_2O_6] \cdot nH_2O$, where $n = 26 - 37$.

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STUDY OF THE REACTIONS OF POLYTHIONATES
WITH THE HELP OF LABELED SULFUR

I. REACTION OF TRITHIONATES

A.I. Brodsky and R.K. Eremenko

Many studies have been devoted to the reactions of formation and decomposition of polythionates. The complex processes of their transformations with participation of sulfides, sulfites, thiosulfates and elemental sulfur are not easily amenable to study by the usual chemical methods. Up to now their study has been limited to the determination of the composition of the reacting mixtures, to its change with time and to the isolation of the products formed. These data do not permit us to draw decisive conclusions, as can be seen from the abundance of diverse and contradictory concepts of the course and intermediate steps of these reactions.

The application of isotopic methods is bound to introduce greater clarity into this problem. Up to the time of commencement of our research, only one investigation had been published [1] on the decomposition of tetrathionate with sulfite using labeled sulfur. In 1952-1953 other papers appeared which used this method for studying the reactions of decomposition of tetrathionate with sulfide and with mercuric chloride [2], the decomposition of polythionates with caustic alkali [3], and the formation of sulfur in the Wackenroder reaction [4].

Below are presented the results of a study of the mechanism of reactions of formation of trithionate with the help of radiosulfur.

EXPERIMENTAL

Decomposition of trithionate. Potassium trithionate was prepared by the three methods described below from compounds containing radiosulfur in specific positions. For establishment of their position in the prepared trithionate, the latter was decomposed by boiling with potassium carbonate solution according to the over-all reaction:

$$S_3O_6^{--} + CO_3^{--} = S_2O_3^{--} + SO_4^{--} + CO_2.$$

The distribution of activity in the thiosulfate was found by converting the latter into the silver salt, which was decomposed by boiling with water:

$$S_2O_3^{--} + 2Ag^{+} + H_2O = Ag_2S + SO_4^{--} + 2H^{+}.$$

From previous studies [5, 6] it is known that in this process the outer (sulfide) atom of sulfur of the thiosulfate passes into silver sulfide and the inner (sulfite) atom into sulfuric acid, and also that there is no exchange between both atoms of sulfur either in the thiosulfate itself or in the process of its decomposition. We confirmed this both by special experiments and by the data of Tables 1 and 5 in which the whole activity of the original sulfur passes into the final silver sulfide.

The sulfate resulting from decomposition of the trithionate was precipitated with strontium nitrate. In the first experiments considerable error was introduced due to part of the sulfate remaining in solution and then changing into thiosulfate. In the final experiments the residue of sulfate, following precipitation with $SrSO_4$, was removed from the filtrate by careful addition of $BaCl_2$ until cloudiness no longer appeared. After this, the thiosulfate was precipitated with excess of $BaCl_2$. The precipitated barium thiosulfate was washed with alcohol and dried. A weighed amount of the barium thiosulfate was then dissolved in hot water and converted into sodium thiosulfate by addition of the calculated amount of sodium sulfate. After this the thiosulfate was perfectly pure. All the described operations do not lead to change of the isotopic content since the sulfates do not exchange sulfur with sulfites, thiosulfates [6, 7] and trithionates. We failed to detect any exchange with the latter at 25° after 26 hours.

Measurement of activity. In the first experiments the activity of the precipitates was measured directly; this led to poor reproducibility. In the final experiments the activity of the sulfate resulting from decomposition of trithionate was measured in the form of $SrSO_4$, while that of all the remaining compounds and of elemental sulfur was measured in the form of benzidine sulfate after Carius oxidation. For this purpose, an ampoule containing 15 mg sample, 15 mg NaBr and 0.2 mg conc. HNO_3 was heated 1 hour at 300°; the contents of the ampoule were then dissolved in water and evaporated on a water bath, and the residue dissolved in 10 ml water and 6 ml alcohol. The solution was precipitated with the calculated amount of benzidine chloride solution (5 g in 40 ml 1 N HCl with addition of 50% alcohol to a volume of 250 ml). The precipitate was washed on the filter and dried; 4 mg precipitate was spread out on a small circle of filter paper on a plexiglas support which was then pushed into the groove of a stand fitted with a counter-tube. The reproducibility of the measurements was approximately 2-4%. In the tables are set forth the number of impulses above the background in 5 minutes, calculated for 1 mg sulfur. If the number of impulses above the background did not exceed 30 (for a total number of 3,000-15,000), the activity was considered zero.

Trithionate from sulfur dichloride and bisulfite. Chlorination of active sulfur was undertaken at 200-250°. To the resultant S_2Cl_2 was added a little sulfur, and it was purified by distillation. The 137-138° fraction with addition of 1% carbon was chlorinated at 0°. The excess chlorine was removed by blowing CO_2 through. The trithionate was prepared by the procedure of Stamm and Goehring [8]. SO_2 was passed with cooling into a solution of 16 ml 5 N KOH until the reaction was neutral. To this solution was added in small portions a solution of 2 g active SCl_2 in 30 ml ligroine. Cooled solutions were employed, and during the reaction the temperature did not rise above 10°. At the end of the reaction and on cooling to 0°, the precipitated potassium trithionate was recrystallized from water, washed with alcohol and then with ether, and dried in the air. It did not give reactions for Cl^-, SO_3^{--}, SO_4^{--} and higher polythionates.

Results of two experiments on the preparation and decomposition of trithionate are set forth in Table 1. Decomposition of the individual samples was performed twice. As seen from a comparison in Table 2, the activity of the trithionate was $^1/_3$ of that of the original sulfur. Its decomposition does not give active sulfate and thiosulfate in which the sulfide sulfur is inactive, but the sulfide sulfur has the same activity as the original sulfur. If the latter is assumed to be unity, then the data obtained exactly correspond to the scheme:

$$2\overset{1}{S} + Cl_2 = \overset{1}{S}_2Cl_2; \qquad \overset{1}{S}_2Cl_2 + Cl_2 = 2\overset{1}{S}Cl_2,$$

$$\overset{1}{S}Cl_2 + 2H\overset{0}{S}O_3^{-} = {}^{-}O_3\overset{0}{S}\cdot\overset{1}{S}\cdot\overset{0}{S}O_3^{-} + 2Cl^{-} + 2H^{+},$$

$${}^{-}O_3\overset{0}{S}\cdot\overset{1}{S}\cdot\overset{0}{S}O_3^{-} + CO_3^{--} = \overset{1}{S}\cdot\overset{0}{S}O_3^{--} + \overset{0}{S}O_4^{--} + CO_2,$$

$$\overset{1}{S}\cdot\overset{0}{S}O_3^{--} + 2Ag^{+} + H_2O = Ag_2\overset{1}{S} + \overset{0}{S}O_4^{--} + 2H^{+}.$$

TABLE 1

Trithionate from $\overset{\bullet}{S}Cl_2 + HSO_3^-$

Experiment Number	Activity (impulses in 5 minutes per mg S)						
	Original S (A)	S_2Cl_2 (B₁)	SCl_2 (B)	Trithionate (C)	Sulfate from trithionate (E)	Ag_2S from final thiosulfate (F)	Sulfate from final thiosulfate (G)
Experiment 1a	1705	1700	1675	570	0	1660	0
Experiment 1b						1695	0
Experiment 2a	2840	2795	2825	970	0	2735	0
Experiment 2b						2765	0

TABLE 2

Trithionate from $\overset{\bullet}{S}Cl_2 + HSO_3^-$

Experiment Number	Ratio of activities			
	A/B	A/C	A/F	F/C
Experiment 1a	1.02	2.99	1.03	2.91
Experiment 1b			1.01	2.98
Experiment 2a	1.01	2.93	1.04	2.82
Experiment 2b			1.03	2.85
Taken	1	3	1	3

Trithionate from thiosulfate and sulfur dioxide. For preparation of $Na_2\overset{\bullet}{S}\cdot SO_3$ with labeled sulfur in an external position, a solution of 20 g KOH in 40 ml water was saturated with SO_2 to a weakly acidic reaction, and then the same amount of KOH solution was added. The sulfite content was determined iodometrically. Into the solution was introduced the equivalent amount of pulverized active sulfur which dissolved completely on heating. Traces of SO_3^{--} and SO_4^{--} were precipitated with strontium nitrate and then with a few drops of barium chloride solution. The solution was evaporated up to a precipitation of the thiosulfate which was recrystallized, washed with alcohol and ether, and dried.

TABLE 3

Trithionate from $\overset{\bullet}{S}\cdot SO_3^{--} + SO_2$

Experiment Number	Activity (impulses in 5 minutes per 1 mg S)					
	Original S (A)	Original $Na_2S_2O_3$ (B)	Trithionate (C)	Sulfate from trithionate (E)	Ag_2S from final thiosulfate (F•)	Sulfate from final thiosulfate (G)
Experiment 1a	4390	2215	1070	0	3095	−40
Experiment 1b				−60	3325	0
Experiment 2a	8320	4115	2090	0	6270	0
Experiment 2b				0	6325	0
Experiment 3a	4545	2160	1140	0	(2575)	0
Experiment 3b				0	(2550)	0
Experiment 4a	11880	5930	2865	0	8665	0
Experiment 4b				30	8715	0
Experiment 5	16600	8295	4170	0	12290	0
Experiment 6	5820	2960	1415	0	4290	0

TABLE 4

Trithionate from $\overset{\bullet}{S}\cdot SO_3^{--} + SO_2$

Experiment Number	Ratio of activities			
	A/B	A/C	A/F	F/C
Experiment 1a	1.98	4.10	1.42	2.89
Experiment 1b			1.32	3.11
Experiment 2a	2.02	3.98	1.33	3.00
Experiment 2b			1.31	3.03
Experiment 3	2.10	3.98		
Experiment 4a	2.00	4.15	1.37	3.02
Experiment 4b			1.36	3.04
Experiment 5	2.00	3.98	1.35	2.95
Experiment 6	1.97	3.92	1.29	3.03
Taken	2	4	4/3	3

Trithionate was prepared [9] by passing a strong stream of SO_2 for 1 1/2 hours into a mixture of 0.4 ml saturated SO_2 solution and 2 g solid active thiosulfate with 1 drop of saturated arsenous acid solution. After separation of the precipitated tetrathionate, SO_2 was again passed through and the solution afterwards poured into a solution of 1 g potassium acetate in 1.2 ml water. The precipitated trithonate was purified as described above.

In a series of preliminary experiments, details of which are not given, not all the precautions were observed which ensure freedom of the tested precipitates from impurities. They gave qualitatively the same results as the final precise experiments set forth in Tables 3 and 4. The trithionate has 1/4 the activity of the original sulfur. Its decomposition gives inactive sulfate and thiosulfate containing 3/8 of the activity of the original sulfur. Decomposition of the latter gave inactive sulfate and Ag_2S containing 3/4 of the activity of the original sulfur:

$$\overset{1}{S} + \overset{0}{S}O_3^{--} = \overset{1}{S}\cdot\overset{0}{S}O_3^{--}$$

$$^{-}O_3\overset{0}{S}\cdot\overset{3/4}{S}\cdot\overset{0}{S}O_3^{-} + CO_3^{--} = \overset{3/4}{S}\cdot\overset{0}{S}O_3^{--} + \overset{0}{S}O_4^{--} + CO_2 \;{**}$$

$$\overset{3/4}{S}\cdot\overset{0}{S}O_3^{--} + 2Ag^{+} + H_2O = Ag_2\overset{3/4}{S} + \overset{0}{S}O_4^{--} + 2H^{+}.$$

Trithionate from thiosulfate and hydrogen peroxide. The method of Willstätter [10] with some modifications was employed. To a solution of 3 g labeled $Na_2\overset{\bullet}{S}\cdot SO_3$ in 2.5 ml water was added dropwise with cooling 30% hydrogen peroxide until the alkaline reaction to phenolphthalein had disappeared. With intense cooling a larger proportion of the sulfate came down. The remainder was precipitated by cautious addition of $BaCl_2$ solution. The trithionate was brought down by running in a solution of potassium acetate, and it was purified as described above.

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* The $Na_2S_2O_3$ isolated from decomposition of trithionate gave in experiments 4, 5 and 6 impulses of 4325, 6165 and 2155.

** The degree of formation of trithionate is considered below.

TABLE 5

Trithionate from $\overset{*}{S} \cdot SO_3^{--} + H_2O_2$

Experiment Number	Activity (impulses in 5 minutes per 1 mg S)						
	Original S (A)	Original $Na_2S_2O_3$ (B)	Trithionate** (C)	Sulfate from trithionate (E)	Final $Na_2S_2O_3$ (J)	Ag_2S from final thiosulfate (F)	Sulfate from final thiosulfate (G)
Experiment 1	5330	–	–	1390	–	5225	1225
Experiment 2a	5130	2380	2370	1315	–	4380	1070
Experiment 2b				1255	–	4380	1065
Experiment 3a	2910	1420	1450	860*	–	2800	625
Experiment 3b				880*	–	2880	660
Experiment 4a	6740	3305	3340	1645	3785	6480	1620
Experiment 4b				1650	3865	6560	1585

As we see from Tables 5 and 6, both the trithionate and the simultaneously formed sulfate possessed 1/2 the activity of the original sulfur. Decomposition of the trithionate gave silver sulfide with the activity of the original sulfur and sulfate with 1/4 its activity. This is represented by the scheme:

$$\overset{1}{2S} \cdot SO_3^{--} + 4H_2O_2 = \overset{1/4}{O_3S} \cdot \overset{1}{S} \cdot \overset{1/4}{SO_3^-} + \overset{1/2}{SO_4^{--}} + 4H_2O$$

$$^-\overset{1/4}{O_3S} \cdot \overset{1}{S} \cdot \overset{1/4}{SO_3^-} + CO_3^{--} = \overset{1}{S} \cdot \overset{1/4}{SO_3^{--}} + \overset{1/4}{SO_4^{--}} + CO_2$$

$$\overset{1}{S} \cdot \overset{1/4}{SO_3^{--}} + 2Ag^+ + H_2O = Ag_2\overset{1}{S} + \overset{1/4}{SO_4^{--}} + 2H^+.$$

TABLE 6

Trithionate from $\overset{*}{S} \cdot SO_3^{--} + H_2O_2$

Experiment Number	Ratio of activities						
	A/B	A/C	A/F	A/E	F/G	J/C	J/G
Experiment 1	–	–	1.02	3.83	4.27	–	–
Experiment 2a	2.16	2.16	1.17	3.90	4.09	–	–
Experiment 2b			1.17	4.09	4.11	–	–
Experiment 3a	2.05	2.01	1.04	(3.38)*	(4.47)*	–	–
Experiment 3b			1.01	(3.31)	(4.36)	–	–
Experiment 4a	2.04	2.02	1.04	4.10	4.00	1.13	2.34
Experiment 4b			1.03	4.08	4.14	1.16	2.44
Taken							
	2	2	1	4	4	5/4	5/2

For an unknown reason the activity of sulfate E and G in experiments 1 and 3 differed by 10-20% from the corresponding scheme, but comparison with it of the activity of the remaining substances leaves no doubt about its correctness. In particular, in experiment 4 the final thiosulfate was isolated before hydrolysis and its activity was 1.15 times greater than the activity of trithionate and 2.4 times greater than the activity of sulfate G, whereas the scheme requires ratios of 5/4 and 5/2.

EVALUATION OF RESULTS

Before going on to consider the mechanism of the reactions corresponding to the determined distribution of activities, we must consider to what degree the distribution may be influenced by secondary exchange of sulfur. In all cases the mean activity of the trithionate corresponds to the activity of the products of its decomposition – silver sulfide and sulfuric acid. All these activities are in simple ratios to one another and to the activity of the original sulfur. Furthermore, if the sulfate resulting from decomposition of trithionate had been inactive, then the final sulfate should also be inactive (Tables 1 and 3). All this excludes the possibility of alteration of the isotopic composition in the process of decomposition of trithionate due to exchange of sulfur. This is explained by the fact that the thiosulfate group enters the trithionate and is cleaved off from it without breaking down. Further evidence of this process is adduced below. These conclusions are directly confirmed by the results of a new investigation by Fava [11] which came to our notice only after the conclusion of the present work. Fava found that thiosulfate exchanges thionate sulfur with the middle sulfur of trithionate with a half-life of 12 hours at 25° and that the other atoms of sulfur of both compounds do not participate in the exchange. The same conclusion was also reached by other authors [1]. Consequently the distribution of active sulfur in trithionate proposed in the schemes can be regarded as correct.

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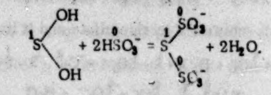
* The separated sulfate evidently contained impurities.

** The separated sulfate, formed at the same time as the trithionate, was contaminated with impurities. In experiments 1, 2, 3, and 4 it had activities of 1825, 1845, 1450 and 2950.

The formation of trithionate by reaction of sulfur dichloride with bisulfite was predicted in 1870 by D. I. Mendeleev [12] and 3 years later was realized by Spring, but it has only recently [8, 13] been studied closely. Its mechanism is not in doubt. Sulfur dichloride is the anhydride of sulfoxylic acid which it forms on hydrolysis:

$$\overset{1}{S}Cl_2 + 2H_2O = \overset{1}{S}(OH)_2 + 2H^+ + 2Cl^-,$$

following which the hydroxyl groups are replaced by sulfite groups:



$$\overset{1}{S}(OH)_2 + 2H\overset{0}{S}O_3^- = \overset{1}{S}(\overset{0}{S}O_3^-)_2 + 2H_2O.$$

This simple mechanism, already put forward by other authors [8, 13), is directly confirmed by the data of Tables 1 and 2. It is in accord with the ideas of D.I. Mendeleev who regarded the polythionic acids as disulfonic acids formed by substitution of the hydrogen in hydrogen sulfides by sulfite groups, for example SH_2 — $S(SO_3H)_2$.

The reaction of sulfites with thiosulfates, as also the analogous reactions in Wackenroder liquid ($H_2S + H_2SO_3$), have been the subject of many investigations in which diverse mechanisms have been advanced. In the majority of contemporary studies the primary formation of sulfur monoxide SO or its hydrate (sulfoxylic acid) is suggested. Further reaction of the latter with sulfites and thiosulfates gives polythionates. An alternative theory is the initial formation of thiosulfurous acid [14, 15], or of hydrogen sulfoxide H_2SO [16]. It has also been suggested that the polythionates primarily formed are trithionate [17], tetrathionate [18, 19, 20], or pentathionate [16, 21], or simultaneously tri- and pentathionate [15, 22], or, finally, tetra- and hexathionate [14]. Equally diverse and conflicting are the equations proposed for these reactions and their steps.

From our results it follows that trithionate is not the primary product of reaction of sulfite with sulfur dioxide, because the central sulfur in trithionate has an activity different from that in all positions in the starting substances. A study of this reaction by chemical methods in presence of As_2O_3 revealed [23] that pentathionate is formed at first and later changes into tetra- and trithionate. Both can be isolated from the reaction mixture in good yield. The distribution of activities that we found exactly corresponds to the following scheme, which is also consistent with the chemical data. The primary product is sulfoxylic acid. Substitution of the hydroxyls in the latter by thiosulfate groups gives pentathionate:

$$\overset{1}{S}\cdot\overset{0}{S}O_3^{--} + 2H^+ + H_2O = 2\overset{1/2}{S}(OH)_2{}^{*}$$

$$\overset{1/2}{S}(OH)_2 + 2\overset{1}{S}\cdot\overset{0}{S}O_3^{--} + 2H^+ = \overset{1/2}{S}(\overset{1}{S}\cdot\overset{0}{S}O_3)_2^{--} + 2H_2O.$$

Successive substitution of thiosulfate groups by sulfite groups gives tetrathionate and trithionate:

$$\overset{1/2}{S}(\overset{1}{S}\cdot\overset{0}{S}O_3)_2^{--} + \overset{0}{S}O_3^{--} = {}^-(O_3\overset{0}{S}\cdot\overset{1/2}{S})\cdot(\overset{1}{S}\cdot\overset{0}{S}O_3)^- + \overset{1}{S}\cdot\overset{0}{S}O_3^{--},$$

$${}^-(O_3\overset{0}{S}\cdot\overset{1/2}{S})\cdot(\overset{1}{S}\cdot\overset{0}{S}O_3)^- + \overset{0}{S}O_3^{--} = {}^-(O_3\overset{0}{S})\cdot(\overset{1}{S}\cdot\overset{0}{S}O_3)^- + \overset{1/2}{S}\cdot\overset{0}{S}O_3^{--},$$

$$\text{or} = {}^-(O_3\overset{0}{S}\cdot\overset{1/2}{S})\cdot(\overset{0}{S}O_3)^- + \overset{1}{S}\cdot\overset{0}{S}O_3^{--},$$

since in tetrathionate both thiosulfate groups are equivalent. In accord with experiments, both routes lead to the mean distribution:

$$= {}^-O_3\overset{0}{S}\cdot\overset{3/4}{S}\cdot\overset{0}{S}O_3^- + \overset{3/4}{S}\cdot\overset{0}{S}O_3^{--}.$$

Isotopic exchange of sulfur between thiosulfate and both the higher polythionates only proceeds by exchange of the whole sulfite or thiosulfate groups. It is easy to see that it can influence the distribution of activity in the trithionate only in the event that the latter stage of its formation has a velocity of the same order as that of the first step of formation of pentathionate, since only in this latter stage does the thiosulfate possess an isotopic composition different from that in the initial step, and it is mixed with the unreacted residue of the latter. The experimentally determined distribution of activity does not reveal an alteration of isotopic composition owing to exchange, evidently the consequence of the great difference in velocities of the two steps in question.*

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* The formation, suggested in some papers by Foerster, of SO or $S(OH)_2$ from HSO_3^- or from $H_2SO_3 + H_2S_2O_3$ is inconsistent with our observations of the distribution of active sulfur.

It should be noted that the primary formation (suggested by other authors) of thiosulfurous acid, which gives tetrathionate [14], or of trithionate from sulfoxylic acid and sulfite [17, 15], or, finally, primary formation of H_2SO [16], are all inconsistent with our data.

In the formation of trithionate from thiosulfate and hydrogen peroxide, in contrast to the two preceding cases, the sulfite (outer) sulfur of trithionate is likewise active. This activity could only be the result of intermediate oxidation of the labeled thionate sulfur of the original thiosulfate to sulfite sulfur. Evidently the only acceptable explanation of our observed distribution of activity is the oxidation of thiosulfate to an ion of a symmetrical acid with two atoms of sulfur – probably dithionic acid:

$$\overset{1}{S}\cdot\overset{0}{S}O_3^{--} + 3H_2O_2 = O_3\overset{1/2}{S}\cdot\overset{0}{S}O_3^{-} + 3H_2O.$$

In the next step the sulfite group is substituted by thiosulfate and is itself oxidized to sulfate:

$$^{-}O_3\overset{1/2}{S}\cdot\overset{0}{S}O_3^{-} + H_2O_2 + \overset{1}{S}\cdot\overset{0}{S}O_3^{--} = {}^{-}O_3\overset{0}{S}\cdot\overset{1}{S}\cdot\overset{1/2}{S}O_3^{-} + \overset{1/2}{S}O_4^{--} + H_2O,$$
$$\text{or } O_3\overset{1/2}{S}\cdot\overset{1}{S}\cdot\overset{0}{S}O_3^{-} + \overset{0}{S}O_4^{--} + H_2O,$$

since exchange of both sulfite groups is equally probable. On the average this gives the observed distribution:

$$^{-}O_3\overset{1/4}{S}\cdot\overset{1}{S}\cdot\overset{1/4}{S}O_3^{-} + \overset{1/2}{S}O_4^{--}.$$

Formally this scheme also satisfies the intermediate formation of persulfate $^{-}O_4S\cdot SO_4^{-}$. Formation of dithionate at the same time as that of trithionate was detected during the Wackenroder reaction in studies by Zilberman [24], although in the latter papers it was attributed to a side reaction of oxidation of sulfite by the analog of hydrogen peroxide–H_2SO. Formation of persulfate by the action of hydrogen peroxide on sulfites and thiosulfates is also known.

The cumulation of the experimental data of the present investigation enables us to confirm that polythionates are built up from sulfite and thiosulfate groups and that the processes of their formation, reciprocal transformations and decomposition proceed by way of addition, exchange or cleavage of these groups. Other investigations using labeled sulfur lead to the same conclusion [1, 3]. The hypothesis that the reversible reactions

$$S_nO_6^{--} + SO_3^{--} = S_{n-1}O_6^{--} + S_2O_3^{--}$$

proceed by transfer of sulfur atoms [25] is incorrect.

The data reported fully confirm the chain-like distribution of sulfur atoms in polythionates and their structure, which was advanced by D.I. Mendeleev.

SUMMARY

1. With the help of labeled sulfur the main reactions of formation of trithionate have been studied.

2. In the preparation of trithionate by the action of sulfur dichloride on bisulfite, the first step is formation of sulfoxylic acid, the hydroxyl groups of which are then substituted by sulfite groups.

3. In the preparation of trithionate by the action of sulfur dioxide on thiosulfate, the first step again is formation of sulfoxylic acid, the hydroxyl groups of which are then replaced by thiosulfate groups with formation of pentathionate. In subsequent steps the substitution of thiosulfate groups by sulfite groups gives tetra- and trithionate.

4. In the preparation of trithionate by the action of hydrogen peroxide on thiosulfate, the first product is a symmetrical product of oxidation of the latter – probably dithionate. Replacement of the latter's sulfite group by thiosulfate gives trithionate.

5. Confirmation is obtained of D.I. Mendeleev's proposed structure of polythionates. The reactions of the latter involve addition, cleavage and exchange of entire sulfite and thiosulfate groups.

6. The incorrectness of the theories advanced in some investigations about the modes of formation and transformations of polythionates is demonstrated.

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* The experimentally established equilibrium $S_5O_6^{--} + S_3O_6^{--} = 2S_4O_6^{--}$, likewise governing the exchange of thiosulfate groups by sulfite groups, can lead only to a difficultly detectable increase in the activity of the middle sulfur of trithionate from 3/4 to 13/16 of the starting activity.

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INVESTIGATION OF THE LIQUIDUS CURVE IN BINARY SYSTEMS FORMED BY THE SODIUM SALTS OF FATTY ACIDS WITH SODIUM NITRATE AND THIOCYANATE

N. M. Sokolov

The properties of sodium salts of fatty acids in melts have not been extensively studied. Thus it comes about that among the large number of binary systems investigated by methods of physicochemical analysis there are no systems comprising salts of fatty acids and sodium nitrate or sodium thiocyanate.

The present research is the first devoted to the examination of this type of system by the method of visual-polythermal analysis. The components of the systems were chosen with a view to comparison of data on the homology and isomerism of salts of fatty acids. To this end we selected salts of formic, acetic, propionic, butyric, caproic, isobutyric and isovaleric acids. With these components it is possible to observe the change of properties of the salts with increasing number of carbon atoms in the radical and with isomerization of the radical.

The fusibility curves of the systems containing nitrate and thiocyanate and an identical fatty acid salt are surprisingly similar. This circumstance prompted us to study the previously uninvestigated system of sodium nitrate – sodium thiocyanate.

The components of the systems – sodium salts of fatty acids [1], sodium nitrate [2] and sodium thiocyanate [3] – melt without decomposition. Certain components can even be heated above their melting points. Thus, formate tolerates heating to 310° [4], acetate to 390° [5], and nitrate to 380° [2], while the thiocyanate does not decompose even when heated to 500° [3].

The literature reports explosion of a mixture of potassium nitrate and sodium acetate on heating [6]; elsewhere the flammability of a heated mixture of sodium thiocyanate and sodium nitrate is reported [7]. We carried out heating of a mixture of salts of fatty acids and sodium nitrate up to 400° and no explosion resulted; mixtures of sodium nitrate and thiocyanate melted quietly and did not inflame at 330-340°. On strong superheating, however, of the melt of a mixture of fatty acid salt and nitrate, gas first began to come off, the temperature rose sharply and, finally, there was an intense flash. This occurs at temperatures at which sodium nitrate decomposes with evolution of gases – oxygen and oxides of nitrogen [8]. It is possible that the cause of the explosions, flashes and inflammations is the reaction of the gaseous products of decomposition of the nitrate with salts of fatty acids and thiocyanates.

Salts of fatty acids with up to four carbon atoms in the radical in admixture both with nitrates and thiocyanates give transparent melts on heating which after solidification satisfactorily withstand repeated remeltings. Systems containing isovalerates and valerates also melted to form transparent liquids, but these had poor stability on remelting and darkened after slight superheating. Systems containing caproate melted to form dark liquids in which the development of the first crystals could be observed with difficulty. These systems readily decomposed when superheated. Additions to these systems of sodium acetate stabilized them and enabled study of the ternary systems of caproate, acetate and sodium nitrate, and caproate, acetate and sodium thiocyanate.

EXPERIMENTAL

The salts were melted in a test tube which was inserted in a broader test tube to ensure more uniform heating. Use was made of a nichrome-constantan thermocouple and a millivoltmeter with mirror reading to 17 mV. The calibration curve was plotted from the following melting points: water 0°, benzoic acid 122°, mannitol 166°, silver nitrate 208°, cadmium 321°, potassium nitrate 337°, and potassium bichromate 398°. On the basis of this calibration curve the melting points of the sodium salts used as components of our systems were: formate 258°, acetate 331°, propionate 298°, butyrate 330°, valerate 357°, caproate 365°, isobutyrate 260°, isovalerate 262°, nitrate 308°, and thiocyanate 311°.

The investigation was carried out with commercial preparations of sodium nitrate and thiocyanate, while the remaining salts were synthesized, starting from the fatty acids and sodium bicarbonate. Commercial sodium nitrate was purified by the method of Laiti* [9]. Sodium thiocyanate (pure for analysis) was twice recrystallized, first from

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* Translator's note: Spelling doubtful (unable to trace).

TABLE 1

Systems of sodium salts of fatty acids and sodium nitrate

Sodium nitrate (in mole-%)	Temperature of start of crystallization in systems formed by							
	Formate	Acetate	Propionate	Butyrate	Isobutyrate	Valerate	Isovalerate	Caproate
0	258	331	298	330	260	357	262	365
5	252	328	294	329	248	366	273	376
10	242	324	291	325	242	372	280	383
15	232	318	287	315	238	369	280	385
25	214	304	282	283	219	350	265	375
27	–	–	–	276	–	–	–	–
30	206	296	280	274	233	336	257	367
31.2	–	–	–	–	–	–	254	–
35	198	286	276	273	244	320	260	357
40	192	276	273	271	258	296	272	342
40.5	–	–	–	–	–	295	–	–
45	188	263	269	268	267	294	282	326
49	186	–	–	–	–	–	–	–
50	190	247	264	267	274	295	288	313
55	206	233	258	276	276	288	294	296
56.5	–	–	255	–	–	–	–	287
58	–	224	–	–	–	–	–	–
58.5	–	–	–	–	–	291	–	–
59	–	–	–	–	–	–	–	300
60	220	231	261	283	280	285	299	302
65	235	242	270	288	284	293	302	–
75	262	264	280	296	288	298	304	Layer formation from 60 to 99.84% sodium nitrate
85	284	284	290	298	292	300	306	
95	302	304	301	302	300	305	307	
100	308	308	308	308	308	308	308	

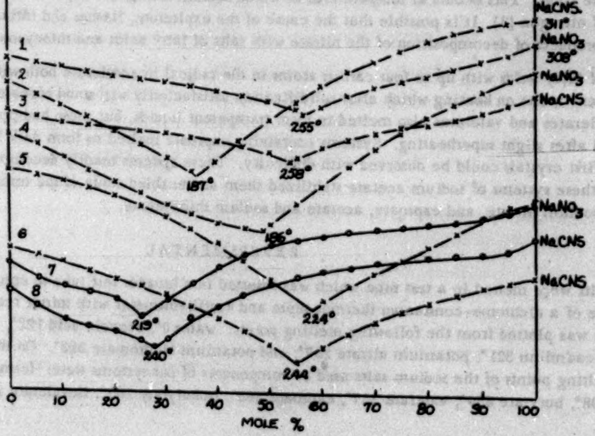

Fig. 1. Liquidus curves of the systems. Sodium nitrate – sodium propionate (1), – sodium formate (4), – sodium acetate (5), – sodium isobutyrate (7); sodium thiocyanate – sodium formate (2), – sodium propionate (3), – sodium acetate (6), – sodium isobutyrate (8).

TABLE 2

Systems of sodium salts of fatty acids and sodium thiocyanate

Sodium thiocyanate (in mole-%)	Temperature of start of crystallization in systems formed by:							
	Formate	Acetate	Propionate	Butyrate	Isobutyrate	Valerate	Isovalerate	Caproate
0	258	331	298	330	260	357	262	365
5	250	326	292	328	247	370	277	383
10	241	320	289	324	237	378	287	397
15	233	313	287	316	231	375	288	399
25	213	302	282	291	221	356	270	386
27.4	–	–	–	–	214	–	–	–
30	202	295	280	275	221	344	256	377
31.5	–	–	–	268	–	–	–	–
32	–	–	–	–	–	–	250	–
35	190	287	276	266	240	331	260	366
36	187	–	–	–	–	–	–	–
40	197	278	273	264	255	316	272	352
45	212	268	270	263	266	296	285	342
46	–	–	–	–	–	289	–	–
48.5	–	–	–	262	–	–	–	–
50	232	256	265	269	274	291	291	330
54	–	–	258	–	–	–	–	–
54.5	–	244	–	–	–	–	–	–
55	244	245	261	280	280	288	297	316
56.5	–	–	–	–	–	287	–	–
60	256	258	269	287	284	290	300	305
63	–	–	–	–	–	–	–	295
65	267	266	276	290	288	293	303	297
75	284	282	285	298	295	297	305	304
90	302	302	298	304	300	302	306	307
100	311	311	311	311	311	311	311	311

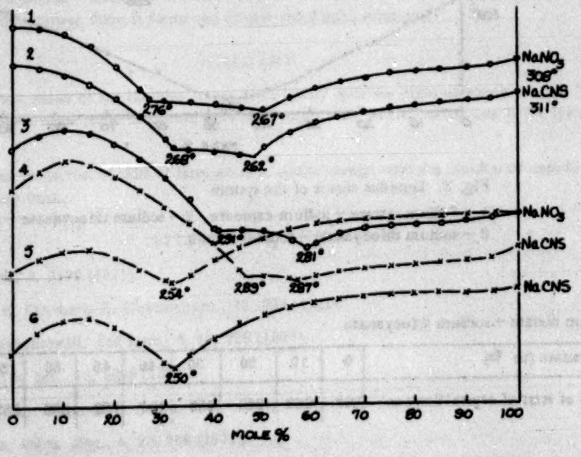

Fig. 2. Liquidus curves of the systems. Sodium nitrate – sodium butyrate (1), – sodium valerate (3), – sodium isovalerate (5); sodium thiocyanate – sodium butyrate (2), – sodium valerate (4), – sodium isovalerate (6).

TABLE 3

Intersection of branches of liquidus curves

Systems	Temperature	$NaNO_3$ (in mole-%)	Temperature	NaCNS (in mole-%)
Formate	186°	49	187°	36
Acetate	224	58	244	54.5
Propionate	255	56.5	258	54
Butyrate E•	267	50	262	48.5
Butyrate P••	276	27	268	31.5
Isobutyrate	219	25	240	27.4
Valerate E_1	291	40.5	289	46
Valerate E_2	281	58.5	287	56.5
Isovalerate	254	31	250	32
Caproate	287	56.5	295	63

• E – eutrectic point
•• P – transition point

water and then from alcohol; its crystals are very hygroscopic; it is more convenient to melt it before use. The thiocyanate melts at 311°; according to the literature it has m.p. 287° [10] and 326° [11]. We failed to obtain a a salt with the higher melting point by synthesizing it from ammonium thiocyanate and caustic alkali or by recrystallization, or by precipitation with ether from a saturated alcoholic solution.

The experimental data are set forth in the tables, and the liquidus curves are plotted in three diagrams.

The liquidus curves of systems formed with sodium salts of fatty acids and sodium nitrate show that in systems containing formate, acetate and propionate there is no complex formation; complex formation is observed in systems containing salts of n-butyric and n-valeric acids. There is no complex formation in systems containing salts of isobutyric and isovaleric acids. Sodium caproate and sodium nitrate have limited mutual solubility in the melted state, and since sodium stearate does not mix at all with sodium nitrate, we can assume that

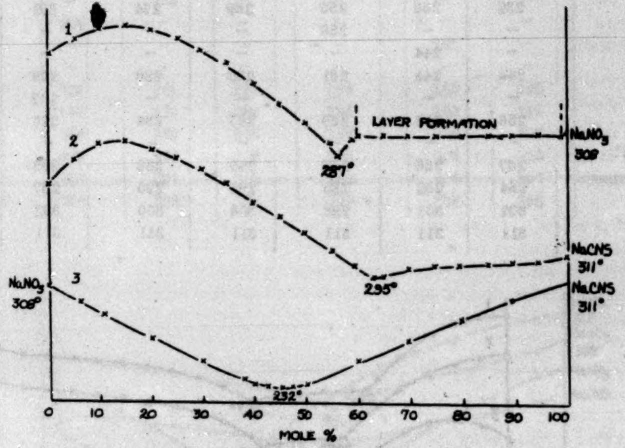

Fig. 3. Liquidus curves of the system
1 – Sodium nitrate – sodium caproate, 2 – sodium thiocyanate – sodium caproate, 3 – sodium thiocyanate – sodium nitrate.

TABLE 4

System sodium nitrate – sodium thiocyanate

Thiocyanate (in %)	0	10	20	30	40	45	50	60	70	80	90	100
Temperature of start of crystallization	308	288	268	252	236	232	236	253	269	285	299	311

salts with more carbon atoms in the radical than caproate will be still less miscible with sodium nitrate in the liquid state (Table 3).

Examination of the liquidus curves of systems formed by salts of fatty acids and sodium thiocyanate shows that, just as in the case with systems containing nitrate, complex formation occurs in the butyrate and valerate systems; systems formed from formate, acetate, propionate, caproate, isobutyrate and isovalerate are characterized by eutectic melting (Table 3).

The great similarity between systems containing thiocyanate and nitrate and the same fatty acid salt makes it interesting to investigate the liquidus curve (not previously studied) of the system sodium nitrate – sodium thiocyanate.

The liquidus curve (Fig. 3) has one branch. In the system is formed a continuous series of solid solutions with a minimum at 232° and 45% sodium thiocyanate.

EVALUATION OF RESULTS

Sodium nitrate and thiocyanate have very similar melting points (308 and 311°) and form a continuous series of solid solutions. Comparison of the liquidus curves of systems containing nitrate with the liquidus curves of systems containing thiocyanate show that when the same fatty acid salt is present in these systems they actually exhibit great similarity. On this basis it is suggested that identical processes take place in such systems during crystallization.

On considering the systems in the order of increasing number of carbon atoms in the radicals of the fatty acid salt component, we see that complex formation does not occur when the paraffinic portion of the molecule is of small size. With increasing number of carbon atoms in the radicals of normal structure, ability to form complexes is first developed and then disappears. Thus caproate does not form compounds either with nitrate or thiocyanate, while sodium stearate is not miscible with them at all.

On comparing systems formed by butyrate and valerate with those formed by isobutyrate and isovalerate, we see that salts containing a branched chain of carbon atoms in the radical do not form compounds; they also possess lower melting melting points than salts of normal structure.

The branches of primary crystallization in the case of isovalerate, valerate and caproate are very similar among themselves. In all cases with increasing content of nitrate or thiocyanate the curve at first rises, reaches a certain maximum and then descends. Such a type of curve with a maximum at the branch of one of the components points to the presence of one-sided solid solutions, as had previously been experimentally demonstrated for the systems sodium sulfate – calcium sulfate [12], silver chloride – cadmium chloride [13], and others. It is possible that also in our systems containing isovalerate, valerate and caproate there is formation of one-sided solid solutions.

SUMMARY

1. An investigation was made of the liquidus curves of 17 binary systems, eight of which contain fatty acid salts and sodium nitrate, eight contain the same fatty acid salts and sodium thiocyanate, while one is the system sodium nitrate – sodium thiocyanate.

2. It is shown that the properties of salts of fatty acids in melts change with the number of carbon atoms in the radical and with the isomeric form.

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THE SYSTEM ACETIC ANHYDRIDE – NITRIC ACID

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Mixtures of nitric acid and acetic anhydride are used for nitration of organic compounds. The main value of such mixtures is that nitration can be effected usually at low temperatures. The absence under these conditions of processes of oxidation and of nitration to polynitro compounds enables purer products to be obtained, and the yields are higher than when nitrating in presence of sulfuric acid. A second advantage is that when such mixtures are used to nitrate aromatic hydrocarbons which are already substituted, the yield of o-nitro compounds is considerably higher than after nitration in any other medium. In individual cases (nitration of aniline), the amount of o-isomer is nearly 100%. Finally, it is possible with such mixtures to obtain products which cannot be obtained under the usual nitration conditions (nitro derivatives of phenanthrene, anthracene and hydroxycarbazole).

The first steps in the examination of the system acetic anhydride – nitric acid were taken by Pictet [1, 2] who suggested that acetyl nitrate was formed in mixtures of acetic anhydride and nitric acid and diacetylorthonitric acid in mixtures of acetic and nitric acids.

In subsequent investigations of the kinetics of nitration of benzene, it was suggested that nitric acid reacts with the solvent [3].

Renewed interest has been shown in recent years in the system acetic anhydride–nitric acid. On the basis of measurements of the vapor tension the hypothesis was advanced of the formation in the system of acetyl nitrate and nitrogen pentoxide [4]. Chedin and Fénéant [5] confirmed this hypothesis by data for the Raman spectra of mixtures of acetic anhydride and nitric acid. The authors considered the formation of nitrogen pentoxide to be the primary step and that of acetyl nitrate the second step in the process

$$2NO_3H + Ac_2O \rightleftharpoons N_2O_5 + 2AcOH, \tag{1}$$

$$N_2O_5 + Ac_2O \rightleftharpoons 2AcONO_2. \tag{2}$$

In a study of the mechanism of nitration of aromatic hydrocarbons, Gold, Hughes and Ingold [6] arrived at the following reversible reactions:

$$HNO_3 + Ac_2O \rightleftharpoons AcOH + AcNO_3, \tag{3}$$

$$HNO_3 + AcNO_3 \rightleftharpoons AcOH + N_2O_5. \tag{4}$$

For investigation of the system acetic anhydride–nitric acid we prepared mixtures of acetic anhydride and nitric acid of strictly specific percentage composition.

The nitric acid needed for their preparation was purified by vacuum distillation by Mishchenko's method [7].

We made a slight modification when assembling the distillation apparatus. The nitric acid which did not condense was absorbed by water in 2 to 3 wash bottles. In front of the first wash bottle (bubbler for nitric acid) was arranged a sulfuric acid wash bottle to protect the nitric acid against access of moisture when air was blown into the system. Distillation was carried out with a water jet pump. Acid containing 99.80÷99.90% nitric acid was used. The concentration of the nitric acid was determined by titration with 0.5N alkali solution in presence of phenolphthalein. The absence of lower oxides of nitrogen in the nitric acid was checked with potassium permanganate.

The acetic anhydride and acetic acid were purified by repeated distillation of the technical product in a column. The fraction of acetic anhydride selected had b.p. 139-140° at 760 mm, and the acetic acid fraction had b.p. 117.4-117.8° at 753 mm.

After preparation, the solutions of nitric acid and acetic anhydride were kept in ice in the course of several hours' working with them.

The atomic concentration* of the system [8 - 10] and the magnitude of ΔA, which represents the difference between the optimum values of the atomic concentration and its additive values, were calculated for the temperature of 0°. The density of the individual mixtures required for the calculation was determined in a pycnometer with a capillary or in a pycnometer with a graduated scale. Determinations were carried out in a thermostat. The temperature was maintained between 0.05 and 0.15°.

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* Translator's note. The atomic concentration is the total number of gram-atoms per liter.

Density (without corrections) was obtained from the weight in air. Correction for the weight had no effect at all on the magnitudes of ΔA and Δd which were of interest to us in this research.

The experimental values of the density of solutions of the system $(CH_3CO)_2O-HNO_3$ (d), the deviations of atomic concentration from the additive values (ΔA), and the magnitudes required for their calculation — the experimental atomic concentration (A) and the additive density (d_u) — are set forth in Table 1.

TABLE 1

Density and atomic concentration of the system $(CH_3CO)_2O-HNO_3$ at 0°.

Composition of mixture (in volume-%)		d, g/ml	d_u, g/ml	Δd, g/ml	A_u	ΔA
HNO_3	$(CH_3CO)_2O$					
0.00	100.00	1.1011	1.1011	0.0000	140.2	0.0
5.62	94.38	1.1167	1.1262	−0.0095	139.2	−1.2
7.55	92.45	1.1245	1.1347	−0.0102	138.9	−1.3
10.12	89.88	1.1327	1.1462	−0.0135	138.4	−1.6
14.97	85.03	1.1484	1.1678	−0.0194	137.6	−2.3
22.84	77.16	1.1751	1.2029	−0.0287	136.2	−3.2
30.11	69.89	1.2025	1.2352	−0.0327	135.0	−3.6
35.01	64.99	1.2231	1.2570	−0.0339	134.1	−3.6
40.00	60.00	1.2473	1.2792	−0.0319	133.2	−3.3
45.82	54.18	1.2763	1.3052	−0.0289	132.2	−2.9
52.04	47.96	1.3072	1.3329	−0.0257	131.1	−2.5
58.96	41.04	1.3453	1.3637	−0.0184	129.9	−1.8
66.85	33.15	1.3943	1.3988	−0.0045	128.5	−0.4
74.68	25.32	1.4515	1.4337	0.0178	127.1	1.6
79.89	20.11	1.4881	1.4569	0.0312	126.2	2.6
82.60	17.40	1.5028	1.4690	0.0322	125.8	2.8
85.04	14.96	1.5122	1.4799	0.0323	125.3	2.7
90.08	9.92	1.5200	1.5023	0.0177	124.5	1.5
100.00	0.00	1.5465	1.5465	0.0000	122.7	0.0

The dependence of ΔA on the composition of the system is plotted in Fig. 1; in the same diagram is plotted the isotherm of Δd. The shape of the isotherm of ΔA, obtained by us for the system $(CH_3CO)_2O-HNO_3$, is a fairly common form of the composition–property curve with a maximum and a minimum. The position of the minimum corresponds almost exactly to the composition of a mixture of 1 mole acetic anhydride and 1 mole nitric acid; hence it is difficult to account for the formation of a minimum solely on the basis of dissociation of the associated component. Moreover, in the literature we failed to find any indication of the association of acetic anhydride molecules. We suggest that the minimum of the ΔA isotherm is due to formation of acetyl nitrate in the system

$$(CH_3CO)_2O + HNO_3 \rightleftharpoons CH_3COONO_2 + CH_3COOH. \qquad (5)$$

Since the number of molecules in the system remains unchanged in formation of acetyl nitrate, the spread must be attributed to the less electrovalent character of the products on the right-hand side of the equation.

The maximum, which corresponds to the molar ratio of nitric acid to acetic anhydride, is equal to 11:1, and it adequately reflects the sharp structural change in the system since only one mole of acetic anhydride per 11 moles acid results in the very high value of ΔA = 2.8 g-at/1. Above all we consider it necessary to draw attention to the fact that acetic acid, which is formed when acetyl nitrate is formed in the system and which is reported in the literature to react with nitric acid, cannot in this range of concentrations give such a large deviation of atomic concentration.

The system acetic acid—nitric acid has been studied in detail by Miskidzhyan and Trifonov [11 - 13], as well as by Naumova [14]. However, these authors were not directly concerned with the study of the density of the system acetic acid—nitric acid at 0°; hence the accuracy of the density values taken from their papers could not satisfy us.

Results of investigations of the system $CH_3COOH-HNO_3$ are set forth in Table 2 and plotted in Fig. 2.

If we now regard the positive values of ΔA in the system acetic anhydride—nitric acid as the consequence of formation of acetic acid, then we must assume that our isotherm of ΔA (Fig. 1) is the sum of two curves, the first of which reflects the formation of acetyl nitrate and moves downwards from the abscissas, while the second reflects the result of interaction of acetic acid with nitric acid and moves upwards from the abscissas. The observed maximum is in this sense only cut off by the end of the upper curve. It should follow from this, however, that the maximum value of ΔA of the system acetic acid—nitric acid at 0° must be very high. Actually, we did

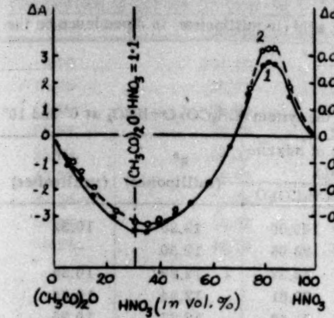


Fig. 1. ΔA (1) and Δd (2) of the system $(CH_3CO)_2O-HNO_3$ at 0°.

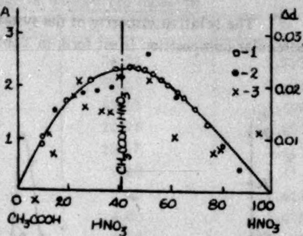


Fig. 2. ΔA and Δd of the system $CH_3COOH-HNO_3$ at 0°. 1) ΔA from the data of our measurements; 2) ΔA from data of Miskidzhyan and Trifonov; 3) Δd from data of Naumova.

TABLE 2

Specific gravity and atomic concentration of the system $CH_3COOH-HNO_3$ at 0°

Composition of mixture (in volume-%)		d,g/ml	d_u,g/ml	Δd ,g/ml	A_u	ΔA
HNO_3	CH_3COOH					
0.00	100.00	1.0708	1.0708	0.0000	142.65	0.0
10.11	89.89	1.1260	1.1189	0.0071	140.6	0.9
10.13	89.87	1.1270	1.1190	0.0080	140.6	1.0
20.08	79.92	1.1808	1.1664	0.0144	138.7	1.7
29.91	70.09	1.2320	1.2132	0.0188	136.7	2.1
39.83	60.17	1.2822	1.2604	0.0218	134.7	2.3
44.76	55.24	1.3065	1.2838	0.0227	133.7	2.4
47.82	52.18	1.3213	1.2984	0.0229	133.1	2.4
50.85	49.15	1.3358	1.3128	0.0230	132.5	2.3
53.90	46.10	1.3499	1.3273	0.0226	131.9	2.3
57.04	42.96	1.3642	1.3423	0.0219	131.3	2.1
59.60	40.40	1.3758	1.3545	0.0213	130.8	2.1
62.98	37.02	1.3905	1.3706	0.0199	130.1	1.9
66.02	33.98	1.4042	1.3850	0.0192	129.5	1.8
69.99	30.01	1.4211	1.4039	0.0172	128.7	1.6
74.90	25.10	1.4419	1.4273	0.0146	127.7	1.3
80.15	19.85	1.4624	1.4523	0.0101	126.7	0.9
100.00	0.00	1.5468	1.5468	0.0000	122.7	0.0

not observe this (Figs. 1 and 2). The ordinate of the maximum of the isotherm of ΔA in the system acetic anhydride–nitric acid is 2.8 g-at/l, and the position of the maximum corresponds to the ratio of acetic acid separated on formation of acetyl nitrate to the acetic acid not bound as acetyl nitrate. This ratio is 1:1.0. but the ordinate of ΔA in the system acetic acid–nitric acid in the corresponding field of concentrations is only 0.6 g-at/l. Consequently, the maximum of the isotherm of ΔA in the system acetic anhydride–nitric acid cannot be accounted for by interaction with nitric acid of the acetic acid formed in the systhem.

We are of the opinion that in this part of the system nitrogen pentoxide is formed, and below we advance considerations about the possible mechanism of its formation.

In comparing the isotherms of ΔA and Δd of the system acetic anhydride–nitric acid (Fig. 1), we must mention that the maximum of both curves corresponds substantially to one and the same composition of the system – 82-83 vol.-% HNO_3. The minimum of the isotherms in both cases also corresponds to an identical concentration of nitric acid (35 vol.-%). This is clear evidence that both of the processes taking place in the system are not complicated by side reactions of the products formed with the starting components of the mixture, and it may serve as confirmation of the fact that acetyl nitrate is by no means an intermediate compound in the process of formation of nitrogen pentoxide.

The viscosity of mixtures of the system acetic anhydride–nitric acid was measured in an Oswald viscometer of the usual type. During the period of keeping of the viscometer in the thermostat with mixtures of one or the other component of the mixture, a rubber tube with screw clips was placed over it to protect the contents against access of moisture.

Determinations were carried out at 0° and 10°. Determinations at 10° were carried out in the course of 20-25 minutes. Prior to these measurements the mixtures were kept, as usual, at a temperature not higher than 0°, so that during the period of determination no far-reaching decomposition of the system was observed.

The relative viscosity of the system acetic anhydride–nitric acid (in millipoises) in dependence on the molecular composition is set forth in Table 3 and plotted in Fig. 3.

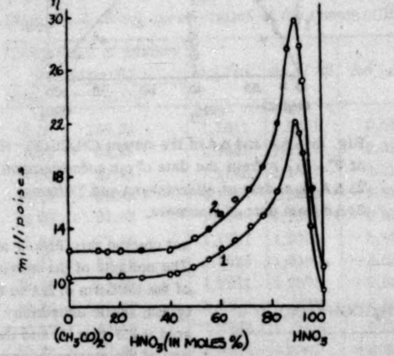


Fig. 3. Viscosity of the system acetic anhydride–nitric acid $(CH_3CO)_2CO-HNO_3$. 1) 10°, 2) 0°.

TABLE 3

Viscosity of the system $(CH_3CO)_2O-HNO_3$ at 0° and 10°

Composition of mixture (in mole-%)		η^0 (millipoises)	η^{10} (millipoises)
HNO_3	$(CH_3CO)_2O$		
0.00	100.00	12.28	10.32
11.94	88.06	12.30	–
15.68	84.32	12.29	10.38
20.39	79.61	12.34	10.40
28.60	71.40	12.27	10.35
40.25	59.75	12.40	10.43
42.98	57.02	–	10.64
45.36	54.64	12.76	–
49.51	50.49	13.09	11.03
55.07	44.93	13.98	11.63
60.27	39.73	15.03	12.45
65.81	34.19	16.04	13.13
71.17	28.83	16.92	14.07
76.57	23.43	–	14.92
76.69	23.31	18.51	–
82.11	17.89	21.84	16.72
87.03	12.97	27.50	20.31
90.04	9.96	29.63	21.96
91.53	8.47	27.86	21.20
92.82	7.18	25.11	19.66
92.38	4.62	16.97	14.08
100.00	0.00	10.99	9.35

The viscosity isotherms contain small but well-marked maxima in the right-hand portion of the diagram. The position of the maxima in relation to the abscissas corresponds to 90 mole-% nitric acid, i.e., approximately the same composition of system as for the maximum of atomic concentration. On raising the temperature to 10° the absolute magnitude of the maximum falls slightly, but its position in relation to the abscissas remains unchanged. On the left hand part of the diagram the isotherms have a direction parallel to the abscissas with an inflection in the curve in the range of 40-50 mole-% HNO_3.

In our opinion the maximum of the isotherms marks the formation in the system of the maximum amount of nitrogen pentoxide. The formation of acetyl nitrate, however, is not accompanied by considerable changes of the viscosity of the system.

The refractive index of the system acetic anhydride–nitric acid was measured in an Abbe refractometer (a saccharimeter with stationary prisms). Measurements were performed at 0-0.5°. Owing to inability to reduce the temperature variations to a lesser degree, the accuracy of our determinations does not exceed $5 \cdot 10^{-4}$.

In Table 4 are set forth the refractive indices in dependence on composition. In Fig. 4 is plotted the isotherm of the refractive index (curve 1). The curve of deviation from additivity (curve 2) exhibits more definitely a minimum in respect to the abscissas at 50 mole-% HNO_3 and a maximum at a concentration of 91 mole-%.

For explanation of the suggested processes we think the most probable assumption is that the molecule of acetic anhydride behaves like a base in presence of nitric acid, adding on a proton to form an acetic anhydride cation $-(CH_3CO)_2OH^+$. This cation then dissociates into acetic acid and acetyl ion. The latter reacts with nitrate ion to form another molecule of acetyl nitrate:

$$(CH_3CO)_2O + HNO_3 \rightleftharpoons (CH_3CO)_2OH^+ + NO_3^-, \quad (6a)$$

$$(CH_3CO)_2OH^+ \rightleftharpoons CH_3CO^+ + CH_3COOH, \quad (6b)$$

$$\underline{CH_3CO^+ + NO_3^- \rightleftharpoons CH_3COONO_2,} \quad (6c)$$

$$(CH_3CO)_2O + HNO_3 \rightleftharpoons CH_3COONO_2 + CH_3COOH \quad (6)$$

TABLE 4
Refractive index of the system $(CH_3CO)_2O-HNO_3$

Composition of mixture (in mole-%)		n_D^0	Composition of mixture (in mole-%)		n_D^0
HNO_3	$(CH_3CO)_2O$		HNO_3	$(CH_3CO)_2O$	
0.00	100.00	1.3993	66.79	33.21	1.3975
11.29	88.71	1.3975	73.88	26.12	1.4010
20.16	79.84	1.3965	77.13	22.87	1.4025
27.87	72.13	1.3959	84.35	15.65	1.4077
35.69	64.31	1.3949	87.85	12.15	1.4117
43.77	56.23	1.3935	90.18	9.82	1.4145
49.36	50.64	1.3936	92.94	7.06	1.4122
55.48	44.52	1.3942	95.40	4.60	1.4082
59.95	40.05	1.3960	100.00	0.00	1.4055

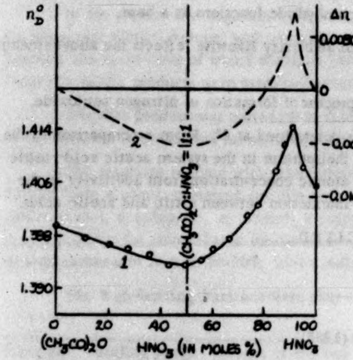


Fig. 4 Refractive index of the system $(CH_3CO)_2O-HNO_3$.
1) n_D, 2) Δn.

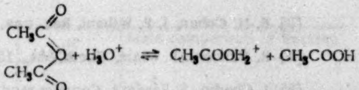
Even an insignificant amount of acetyl cation in the system proves sufficient for formation of acetyl nitrate.

On the basis of the ΔA diagram we must conclude that the process of formation of acetyl nitrate proceeds substantially completely from left to right at equimolecular concentration of components and becomes extremely insignificant at a nitric acid concentration of 80-90 mole-%.

In the region of predominating concentrations of nitric acid we suggest that nitrogen pentoxide is formed.

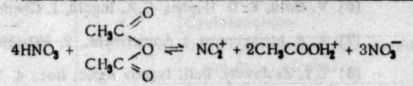
We consider the formation of nitrogen pentoxide in the system to be possible in accordance with the following scheme:

$$3HNO_3 \rightleftharpoons H_2O^+ NO_2^+ + 2NO_3^-, \qquad (7a)$$



$$(CH_3CO)_2O + H_3O^+ \rightleftharpoons CH_3COOH_2^+ + CH_3COOH \qquad (7b)$$

$$CH_3COOH + HNO_3 \rightleftharpoons CH_3COOH_2^+ + NO_3^-, \qquad (7c)$$



$$4HNO_3 + (CH_3CO)_2O \rightleftharpoons NO_2^+ + 2CH_3COOH_2^+ + 3NO_3^- \qquad (8)$$

$$NO_2^+ NO_3^- \rightleftharpoons N_2O_5 \qquad (9)$$

$$2CH_3COOH_2^+ + 2NO_3^- \rightleftharpoons 2CH_3COOH + 2HNO_3 \qquad (10)$$

According to current ideas about the dissociation of nitric acid and its aqueous solutions, close to 100%, equilibrium (7a) also exists in nitric acid as such. On adding acetic anhydride to nitric acid, the former reacts with the hydroxonium ion to form a molecule of acetic acid and a cation of acetic acid (7b). The formed molecule of acetic acid removes from the system the subsequent molecule of nitric acid (7c). The over-all equation of the proposed reactions is represented by equation (8). Equilibria (9) and (10) are possible for the products of the right-hand side of this equation. Equation (9) represents the process of formation of nitrogen pentoxide in the system. The process of formation of the undissociated form of nitrogen pentoxide and the process expressed by equation (7b) shift the reaction of dissociation of nitric acid to the right. With excess of nitric acid, the disturbed state will be restored by dissociation of the subsequent molecules of nitric acid of the acid-base type.

From the ΔA diagram it follows that the maximum shift of the process expressed by equation (7a) to the right (maximum concentration of nitrogen pentoxide) occurs at a concentration of 91 mole-% nitric acid. On the viscosity diagram the process of formation of nitrogen pentoxide is characterized by a maximum in the region of 90 mole-%; on the refractive index diagram it is marked by a maximum for the mixture containing 91 mole-% nitric acid.

Consequently, contrary to the view of Chedin and Fénéant, on the one hand, and to the view of Gold, Hughes and Ingold on the other hand, we suggest that, in dependence on the ratio of concentrations of starting components, either the reversible process of reaction of acetic anhydride with nitric acid, with formation of acetyl nitrate, or the process of formation of nitrogen pentoxide due to reaction of nitric acid with acetic anhydride will prevail in the system.

To summarize our observations on the system acetic anhydride–nitric acid, we may say that the atomic concentration and refractive index point both to the formation of acetyl nitrate in the system and to formation of nitrogen pentoxide. The viscosity of the system clearly reflects only the process resulting in formation of nitrogen pentoxide.

SUMMARY

1. Determinations were made of the density at 0°, viscosity at 0° and 10° and refractive index at 0° in the system acetic anhydride–nitric acid.

2. Deviations of the atomic concentration from additivity– ΔA – reveal the occurrence in the system of two equilibrium processes of interaction of acetic anhydride with nitric acid: formation of acetyl nitrate in the region of equimolecular concentrations and formation of nitrogen pentoxide in the region of very high concentrations of nitric acid. In the first stage of both processes, acetic anhydride functions as a base.

3. The isotherm of deviation of the refractive index from additivity likewise reflects the above-mentioned processes.

4. The viscosity of the system clearly reflects only the process of formation of nitrogen pentoxide.

5. The density of the system acetic acid–nitric acid was determined at 0°. From a comparison of the isotherm of ΔA in the system acetic anhydride–nitric acid with the isotherm in the system acetic acid–nitric acid, it follows that such considerable positive deviations of the atomic concentration from additivity in the system acetic anhydride–nitric acid cannot be caused solely by interaction between nitric and acetic acids.

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**** See Consultants Bureau English translation page 1223.

THE REACTION OF ACETONE WITH ANHYDROUS POTASSIUM HYDROXIDE

B. T. Zubakhin

The following reactions between two or three molecules of acetone are known:

1) Condensation under the influence of acids with formation of mesityl oxide, phorone and mesitylene.

2) Condensation under the influence of aqueous solutions of caustic alkalies with formation of diacetone alcohol.

The problem of the mechanism of "resinification" of acetone under the action of anhydrous caustic alkalies in presence of atmospheric oxygen and the formation of an oily product in the absence of air has remained completely unclarified.

In the present investigation we have succeeded in establishing that on reaction of acetone and other ketones (in particular diethyl ketone) with anhydrous granulated potassium hydroxide, formation takes place of an oily product, the main mass of which distils at 150-360° (see table). The product has a pleasant minty-softwood odor. From the acidic products were separated acetic and pyroracemic acid (in the form of their potassium salts).

The oily product was subjected to fractional distillation. In the table are set forth the temperature ranges of the isolated fractions and for some of them the specific gravities and refractive indices.

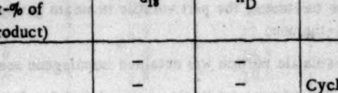
The fractions reacted with semicarbazide acetate, forming semicarbazones which, after many recrystallizations from alcohol, possessed definite melting points, corresponding to the semicarbazones of mesityl oxide, cyclohexanol, d-pulegone, α-thujone, n-isopulegone. On the basis of the yield of semicarbazones it could be concluded that the investigated fractions contained 60-70% keto compounds. After oxidative treatment, the yield of semicarbazones rose to 90-95%, which indicated the presence of 25-35% compounds containing hydroxyl.

The high-boiling fractions were only examined qualitatively.

Fraction number	Boiling range	Weight of fraction (in weight-% of starting product)	d_{18}^{18}	n_D^{21}	Main components of fraction
1	130-170°	–	–	–	
2	170-190	–	–	–	Cyclohexanone
3	190-220	20	0.910	1.494 ± 1	Isopulegol, isopulegone, thujone and thujyl alcohol
4	220-250	16	–	–	Pulegone
5	250-290	32	0.970	1.527	–
6	290-310	8	–	–	–
7	310-360	14	0.990	1.525	–
	Resinous residue	8-10	1.05	–	–

The boiling points of the various fractions set forth in the table, their specific gravity and refractive index, and the preparation from these fractions of semicarbazones with definite melting points demonstrate that in the action of potassium hydroxide on acetone the products were ketones and alcohols identicial with products of the terpene series – mesityl oxide, cyclohexanone, n-isopulegone, α-thujone and, apparently, isopulegol and thujyl alcohol.

These data enable us to advance the following reaction mechanism: At the start two molecules of acetone condense with formation of mesityl oxide. Formation of cyclohexanone may be represented as the consequence of far-reaching rearrangement of mesityl oxide:



Formation of terpene alcohols may be regarded as proceeding according to the following over-all equation:

$$C_6H_{10}O + 2(CH_3)_2CO + KOH \longrightarrow C_{10}H_{18}O + CH_3COOK + H_2O.$$

Ketones of the terpene series are formed by oxidation of terpene alcohols. When the reaction is carried out in absence of air, it evidently stops short at the step of formation of terpene alcohols.

When carrying out the reaction in presence of oxygen of the air, high-boiling products are also formed; on the basis of a series of qualitative tests and of the data set forth in the table, these are sesquiterpenes and diterpenes; at the same time alcohol-soluble and bituminous resins are formed.

EXPERIMENTAL

1. Reaction of acetone with potassium hydroxide. A mixture of 180 ml acetone and 70 g KOH was stood for 7 days at room temperature. The liquid was then decanted from the solid, neutralized, and fractionated to give the fractions shown in the table.

The 1st and 2nd fractions were again subjected to fractional distillation. From the resultant two main fractions could be isolated semicarbazones with m.p. 156 and 166°, which pointed to the presence in the mixture of mesityl oxide and cyclohexanone [1]. From the 3rd and 4th fractions, after fractional distillation and distillation with steam, could be separated several products: a first with b.p. 200-210°, a second with b.p. 210-220°, and a third with b.p. 220-225°.

From the first product was obtained a semicarbazone with m.p. 186°, corresponding to α-thujone [2]. The oily portion of the products which did not react with semicarbazide gave the same semicarbazone after oxidation with chromic acid.

From the third product was obtained a semicarbazone with m.p. 167-168°, corresponding to d-pulegone.

The portions of the 4th fraction non-volatile with steam gave still another semicarbazone with m.p. 182-183°, corresponding to n-isopulegone [3].

Broadly, the same compounds were obtained by boiling acetone in presence of KOH.

Reaction of acetone with KOH on heating in absence of air gave a mobile, oily liquid. No resins or high-boiling derivatives were formed in this reaction. About 5% of semicarbazones were formed.

After oxidative treatment, the part volatile in steam gave two semicarbazones with m.p. 186 and 174°, corresponding to α- and β-thujone.

From the non-volatile portion was obtained isopulegone semicarbazone (m.p. 182-183°).

Consequently, the mixture evidently consisted mainly of thujyl alcohol and isopulegol. In the lower aqueous layer was found about 9% potassium acetate.

When diethyl ketone is stood for a long period with solid, finely granulated potassium hydroxide, a liquid is formed with a pleasant, minty odor. After isomerization in 40% KOH solution, this liquid forms a semicarbazone with m.p. 184°.

SUMMARY

1. It is shown that reaction of acetone with anhydrous KOH in presence of oxygen of the air evidently leads to formation of terpenic alcohols and ketones.

2. Only terpene alchols appear to be formed when acetone reacts with anhydrous KOH in the absence of air.

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CATALYTIC PREPARATION OF MIXED KETONES FROM PRIMARY ALCOHOLS

II. KETONIZATION OF A MIXTURE OF ETHYL AND ISOAMYL ALCOHOLS

B.N. Dolgov and G.V. Golodnikov

In the preceding communication [1] consideration was given to the process of ketonization of a mixture of two primary alcohols of normal structure. It appeared to us of interest to investigate further the characteristics of the ketonization of a mixture of alcohols of normal and iso structure, for example ethyl and isoamyl alcohols. As the results of this work show, on passing such a mixture over the copper-activated catalyst of Dolgov and Bolotov [2], methylisobutyl ketone is obtained in good yield, as well as acetone and diisobutyl ketone in minor amounts.

Optimum conditions for formation of the mixed ketone were established by a study of the influence of temperature, ratio of alcohols in the mixture, space velocity and supplementarily introduced hydrogen.

It follows from experiments with a passage of 1 : 1 (molar ratio) mixture of ethyl and isoamyl alcohols over the catalyst at various temperatures (between 275 and 425°) and constant space velocity (150) that the optimum reaction temperature is 350° (Table 1).

TABLE 1

Experimental temperature	Yields (in % of starting mixture of alcohols)						
	Acetone	Methyl isobutyl ketone	Diisobutyl ketone	Isovaleraldehyde	Esters	Ethyl alcohol	Isoamyl alcohol
			Molar ratio 1 : 1				
275°	0.0	1.0	0.4	12.0	30.4	10.1	23.0
300	3.0	6.2	0.6	5.6	30.9	4.4	20.1
325	2.7	12.0	1.8	3.6	16.4	6.4	11.8
350	2.2	18.5	4.1	4.6	9.0	1.8	7.2
375	0.0	10.7	4.9	11.0	8.4	2.8	4.8
400	0.0	10.7	4.0	14.7	2.8	3.9	7.8
425	0.0	8.6	3.6	10.0	0.7	2.0	18.9
			Molar ratio 1 : 2				
275	0.0	4.1	0.5	13.2	44.7	9.5	26.0
300	0.0	10.1	1.0	12.6	41.7	4.0	25.1
325	0.0	16.0	0.8	3.8	34.7	2.6	12.6
350	0.0	12.0	6.2	7.2	33.8	3.9	9.0
375	0.0	11.7	10.0	8.9	26.4	9.0	5.6
400	0.0	6.0	2.8	16.7	8.7	5.9	10.9
425	0.0	6.5	1.0	11.1	17.5	5.0	13.8
450	0.0	6.3	5.4	7.8	17.2	5.0	21.6
			Molar ratio 2 : 1				
275	2.6	2.3	0.6	9.0	21.0	14.4	9.0
300	0.0	5.0	4.2	5.6	16.3	4.5	3.9
325	0.0	13.3	2.1	4.8	9.0	3.0	3.6
350	1.0	21.0	4.7	0.7	4.0	5.0	1.8
375	0.0	2.8	4.5	4.5	5.0	13.5	4.9
400	0.0	2.6	6.3	1.3	6.4	11.5	8.8

TABLE 2

Space velocity	Yields (in % of starting mixture of alcohols)						
	Acetone	Methyl isobutyl ketone	Diisobutyl ketone	Isovaleraldehyde	Esters	Ethyl alcohol	Isoamyl alcohol
51	0.8	16.4	6.2	0.5	2.1	3.0	3.4
99	0.6	18.0	5.1	0.5	3.0	4.5	2.5
151	1.0	21.0	4.7	0.7	4.0	5.0	1.8
200	2.0	7.0	4.7	16.7	7.0	12.0	8.0
301	3.5	2.6	4.0	7.7	9.4	25.6	8.2

TABLE 3

Experimental conditions	Yields (in % of starting mixture of alcohols)						
	Acetone	Methyl isobutyl ketone	Diisobutyl ketone	Isovaleraldehyde	Esters	Ethyl alcohol	Isoamyl alcohol
In presence of hydrogen	1.0	21.0	4.7	0.7	4.0	5.0	1.8
Without hydrogen							
1st hour	0.0	3.9	2.7	17.4	4.5	12.2	9.4
2nd hour	0.0	3.2	2.1	20.9	5.5	16.9	12.6

The slightly higher optimum temperature in this case in comparison with the temperature of the reaction of formation of methyl propyl ketone (325°) [1] is due to the effect of the branching of one of the starting alcohols.

As we see from Table 1, the best ratio of ethyl and isoamyl alcohols from the standpoint of yield of methyl isobutyl ketone is a molar ratio of 2 :1, at which the mixed ketone is obtained as the main reaction product. Just as in the case of a mixture of ethyl and butyl alcohols, rise of temperature is accompanied by a drop in the yield of esters which at low temperatures reaches 20-45% of the mixed alcohols passed through. The maximum for methyl isobutyl ketone at 350° corresponds to a minimum for isovaleraldehyde. Consequently fresh confirmation is obtained of intermediate formation of aldehydes and esters during ketonization of mixtures of alcohols.

The effect of space velocity on the yields of methyl isobutyl ketone was determined from experiments with a mixture of ethyl alcohol and isoamyl alcohol in the molar ratio of 2 : 1 at 350°, i.e. under the optimum conditions for formation of methyl isobutyl ketone. It follows from inspection of the data of Table 2 that the best yields of mixed ketone are obtained at space velocities of 50-150, further rise of space velocity to 200 sharply reducing the yields. Isovaleraldehyde is obtained in insignificant yield in the region of maximum yields of methyl isobutyl ketone, but its amount rises sharply at a space velocity of 200.

For clarification of the role of hydrogen, a 2 : 1 (molar) mixture was passed over the catalyst at optimum conditions, i.e. at 350° and space velocity of 150°, but in the absence of hydrogen. The experiment was continued for two hours, and the liquid and gaseous products collected after the first and second hour were examined separately. We see from Table 3 that in the absence of hydrogen there is a sharp drop in the yield of methyl isobutyl ketone, accompanied by an equally sharp rise in yield of isovaleraldehyde and a slight rise in the amount of esters.

Performance of the reaction without hydrogen inhibits the steps of condensation of aldehydes to esters and ketones.

EXPERIMENTAL

The ethyl alcohol used in the work was commercial rectified spirit (95%), d^{18} 0.805. The commercial isoamyl alcohol was dried over Na_2SO_4 and distilled: b.p. 130.5-132.0°; d^{18} 0.816 n_D^{18} 1.4080. The experiments were performed in the apparatus used for ketonization of a mixture of ethyl and butyl alcohols [1]. The liquid condensates from each experiment were fractionated in a rectifying column. The following fractions were usually obtained: 1st 54-60°; 2nd 60-80°; 3rd 80-90°; 4th 90-95°; 5th 95-118°; 6th 113-118°; 7th 118-145°; 8th 145-163°; 9th 163-168°; 10th 168-188°; residue (above 188°). Fractions with identical boiling points from all the fractionations were, after analysis, combined and refractionated in a column in order to isolate the individual substances and to identify them.

The first fraction contained acetone and formed not more than 1-2% of the weight of condensates; it was analyzed for its ketone content by the hydroxylamine method.

The 2nd fraction contained ethyl acetate and isovaleraldehyde. C_2H_6O was determined by difference.

The 3rd and 4th fractions contained isovaleraldehyde, which was determined by the ammoniacal silver method, and water.

The 5th fraction consisted of isovaleraldehyde, methyl isobutyl ketone and water. On refractionation, a fraction corresponding to isovaleraldehyde was separated.

b.p. 91.5-92.5°, n_D^{20} 1.3920.
Literature data: b.p. 92.5°, n_D^{20} 1.39225.
The 2,4-dinitrophenylhydrazone melted at 122.5-123.0 (the literature reports 123.0°).
Found %: N 21.12. $C_{11}H_{14}O_4N_4$. Calculated %: N 21.05.

The 6th fraction contained methyl isobutyl ketone which was isolated and identified after refractionation:

B.p. 115.5-116.5°, d_4^{20} 0.8056, n_D^{20} 1.3973.
Found: M 100.3, 98.8. $C_6H_{12}O$. Calculated: M 100.
The recrystallized semicarbazone had m.p. 130.5-131.0° (literature 132.0°).
Found %: N 27.0. $C_7H_{15}ON_3$. Calculated %: N 26.75.

From the 7th fraction on refractionation was separated 129.5-131.0 and 131-143° fractions.

The 129.5-131.0° fraction was isoamyl alcohol.

The 131-145° fraction contained ethyl isovalerate (b.p. 134.7°) and isoamyl acetate (b.p. 142°). Their presence was confirmed by saponification of the fraction with 25% KOH when 2 fractions of organic acids a and b were obtained; from the latter were prepared the silver salts.

Fraction a. Found %: Ag 51.20. C_4H_9COOAg. Calculated %: Ag 51.65.
Fraction b. Found %: Ag 65.23. CH_3COOAg. Calculated %: Ag 64.65.

The 8th fraction was an intermediate one, very small in quantity and containing diisobutyl ketone (identified by analysis).

The 9th fraction contained diisobutyl ketone which was isolated by refractionation and was identified:

B.p. 165-166°, d_4^{20} 0.8274, n_D^{20} 1.4138.
Literature data: b.p. 168°, d_4^{20} 0.8279, n_D^{21} 1.4120.
The recrystallized semicarbazone had m.p. 121-122° (literature: 121-122°).
Found %: N 21.62. $C_{10}H_{21}ON_3$. Calculated %: N 21.11.
The 2,4-dinitrophenylhydrazone melted at 66.0-66.5° (literature: 66°).

The 10th fraction and the residue contained (by analysis) ketones and esters. Refractionation gave fractions corresponding to isoamyl isovalerate:

B.p. 188-190°, d_4^{20} 0.8577, n_D^{20} 1.4136.
Literature data: b.p. 190.4°, $d_4^{18.7}$ 0.8583, $n_D^{18.7}$ 1.41300.
Found: M 168.3, 168.9. $C_{10}H_{20}O_2$. Calculated: M 172.

The composition of the gas from experiments under conditions most favorable for formation of mixed ketone is characterized by a very high content of hydrogen (about 85%); it also contains CO_2 (5-6%) and CO (5-8%). The olefins content of the gas is very small (2-2.5%), saturated hydrocarbons are absent.

SUMMARY

1. In the formation of methyl isobutyl ketone as the main product of reaction over activated copper catalyst, the optimum conditions are a molar ratio of ethyl and isoamyl alcohols in the starting mixture of 2 :1, a temperature of 350°, and a space velocity of 50-150. Under these conditions the yield of methyl isobutyl ketone is 18-21% on the starting mixture, that of acetone is 0.6-1%, and that of diisobutyl ketone about 5%. The overall yield of ketones is not less than 24-26% reckoned on the starting mixture.

2. At low experimental temperatures (275-300°) high yields of esters (up to 45%) are obtained. Among the reaction products are ethyl acetate, isoamyl acetate, ethyl isovalerate and isoamyl isovalerate.

3. The slightly higher optimum temperature for formation of methyl isobutyl ketone in comparison with that for methyl propyl ketone is explained by the effect of the branched structure of one of the starting components.

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The 2nd fraction consisted of [illegible] and [illegible] [illegible] of [illegible].

The 3rd and 4th fractions contained [illegible], which [illegible] the [illegible] and water.

The [illegible] fraction [illegible] at [illegible] [illegible] [illegible] a fraction [illegible] of [illegible] [illegible] temperature.

B.p. [illegible] °, n_D^{20} [illegible]

Literature data: b.p. [illegible] °, n_D^{20} [illegible]

The [illegible] [illegible] [illegible] m.p. [illegible] ° (literature [illegible] [illegible] °).

Found %: [illegible]. $C_{[illegible]}H_{[illegible]}O_4N_4$. Calculated %: [illegible]

The 4th fraction consisted of methyl isobutyl ketone [illegible] [illegible] and [illegible] [illegible] [illegible]

B.p. 115.5-116.5°, d_4^{20} 0.8006, n_D^{20} 1.3970.

Found: M 100.2, [illegible]. $C_6H_{12}O$. Calculated: M 100.

The [illegible] and [illegible] [illegible] m.p. 133.5-134.5° (literature 133.5°).

Found %: [illegible]. Calculated %: [illegible]

From the [illegible] fraction [illegible] [illegible] [illegible] 138.5-139.5° and 150-151° [illegible].

The [illegible] of [illegible] [illegible] [illegible].

The [illegible] fraction contained [illegible] [illegible] [illegible] [illegible] [illegible] and [illegible] [illegible]. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] which a and [illegible] were obtained, and the [illegible] were [illegible] the [illegible].

Fraction a. Found %: Ag 41.90. [illegible]. Calculated %: Ag 41.90.

Fraction b. Found %: Ag [illegible]. [illegible]. Calculated %: Ag [illegible].

The [illegible] of [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] by [illegible].

The 7th fraction [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] and [illegible].

B.p. 155-156°, d_4^{20} [illegible], n_D^{20} [illegible]

Literature data: b.p. [illegible], d_4^{20} [illegible], n_D^{20} [illegible]

The [illegible] [illegible] m.p. [illegible]. Literature [illegible].

Found %: N [illegible]. [illegible]. Calculated %: N [illegible].

The [illegible] [illegible] [illegible] [illegible]. Literature: [illegible].

The 10th fraction and the [illegible] [illegible] [illegible] [illegible] [illegible] and [illegible]. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] temperature.

B.P. 165-166°, d_4^{20} [illegible], n_D^{20} [illegible]

Literature data: b.p. 166-67°, d_4^{20} [illegible], n_D^{20} [illegible]

Found: M [illegible]. [illegible]. Calculated: M [illegible].

The composition of the gas [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] by [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] the content of the gas is [illegible] [illegible] [illegible] [illegible] are shown.

SUMMARY

1. In the formation of methyl isobutyl ketone at the [illegible] [illegible] [illegible] [illegible] copper catalyst the optimum conditions are a [illegible] [illegible] of [illegible] [illegible] [illegible] [illegible] [illegible] of [illegible] [illegible] of 330°, and a space velocity of [illegible]. Under these conditions the yield of methyl isobutyl ketone is [illegible] on the starting mixture, that of acetone is [illegible], and [illegible] [illegible] [illegible]. The overall yield of [illegible] is not less than [illegible] [illegible] on the starting mixture.

2. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] acetic [illegible] [illegible] [illegible] [illegible] [illegible] and [illegible] [illegible].

3. The [illegible] [illegible] [illegible] temperature for [illegible] of methyl isobutyl [illegible] [illegible] [illegible] [illegible] [illegible] by [illegible] [illegible] is explained by the effect of the [illegible] [illegible] of [illegible] of the [illegible] [illegible].

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CATALYTIC SYNTHESIS OF KETONES

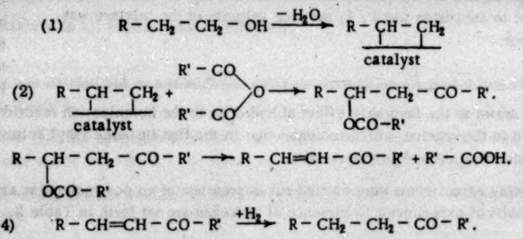
III. SYNTHESIS OF METHYL ETHYL, METHYL-n-BUTYL AND METHYLISOBUTYL KETONES

I.P. Yakovlev and Ya. Dorfman

In preceding communications it was shown that reaction of acetic acid with ethyl alcohol [1] and of acetyl chloride with ethyl bromide gives methyl ethyl ketone [2]; acetic acid and n-butyl alcohol give methyl sec-butyl and methyl n-butyl ketones. At the same time a general scheme was put forward for the catalytic synthesis of ketones [1-3] according to which any two molecules of the type of $R-C\overset{\nearrow O}{\underset{\searrow X}{}}$ and $Y-CH_2-CH_2-R'$ must form a ketone over a catalyst in a specified temperature range in presence of hydrogen. X and Y may be: H, halogens, OH, OR, OCOR, apparently the $N(H, R)_2$ group, etc.

We now continue the investigation and the checking of the theoretical concepts of the mechanism of ketonization advanced previously by one of us [1, 2, 3]. A new method is also submitted for the synthesis of ketones, starting from acetic anhydride and alcohols (ethyl, butyl and isobutyl).

On the basis of the earlier considerations the reaction between an acid anhydride and an alcohol may be represented in the following general form:



$$(1)\quad R-CH_2-CH_2-OH \xrightarrow{-H_2O} \underbrace{R-\underset{|}{C}H-\underset{|}{C}H_2}_{\text{catalyst}}$$

$$(2)\quad \underbrace{R-\underset{|}{C}H-\underset{|}{C}H_2}_{\text{catalyst}} + \begin{matrix} R'-CO \\ R'-CO \end{matrix}\!\!>O \longrightarrow R-\underset{\displaystyle OCO-R'}{\underset{|}{C}H}-CH_2-CO-R'.$$

$$(3)\quad R-\underset{\displaystyle OCO-R'}{\underset{|}{C}H}-CH_2-CO-R' \longrightarrow R-CH{=}CH-CO-R' + R'-COOH.$$

$$(4)\quad R-CH{=}CH-CO-R' \xrightarrow{+H_2} R-CH_2-CH_2-CO-R'.$$

Carboxylic acids may here be formed both by hydrolysis of the anhydride with water released in reaction (1), and by decomposition of the keto ester according to (3).

The experimental work confirms this scheme. Actually there were obtained only those reaction products to be expected from the schemes: 1) from acetic anhydride and ethyl alcohol were obtained acetone and methyl ethyl ketone; 2) from acetic anhydride and n-butyl alcohol were obtained acetone, methyl sec-butyl and methyl n-butyl ketones; 3) from acetic anhydride and isobutyl alcohol were obtained acetone and methyl isobutyl ketone.

EXPERIMENTAL

Starting substances. The acetic anhydride had the following constants: b.p. 139.5°, n_D^{18} 1.3900. The ethyl alcohol was dehydrated with copper sulfate (anhydrous). Final concentration of ethanol 99.5% (by weight); b.p. 78.5°; n_D^{18} 1.3615. n-Butyl alcohol had b.p. 117°; n_D^{20} 1.399. Isobutyl alcohol had b.p. 107°; n_D^{20} 1.397. Hydrogen was obtained by the action of sulfuric acid on zinc free from arsenic, and it was purified with a solution of potassium bichromate in sulfuric acid. The catalyst was prepared from chromic oxide and manganese nitrate [4].

Experiments were carried out in an ordinary laboratory catalytic apparatus. The starting mixture was fed at constant speed from an automatic buret. The catalyst (80 ml), consisting of equal parts by weight of chrome-manganese powder and asbestos wool, was placed in a zone of the furnace with approximately identical temperature. The temperature of the electric furnace was adjusted with a laboratory autotransformer and was measured with a thermocouple in a pyrex case placed in the reaction tube. The required volume of hydrogen was measured with a flowmeter. The gases were passed either to atmosphere or to a gasholder for analysis.

The catalyzate was worked up in the following manner: a) preliminary distillation from a Favorsky flask; b) treatment with calcium chloride for removal of water and alcohol; c) fractional distillation in a laboratory fractionating column. The ketones obtained were identified from their constants and from their semicarbazones and 2,4-dinitrophenylhydrazones. The ketones were quantitatively determined by titration with hydroxylamine hydrochloride in presence of bromophenol blue [5].

1. Synthesis of methyl ethyl ketone from acetic anhydride and ethyl alcohol. Data for experiments in absence of hydrogen are set forth in Table 1.

The data of Table 1 show that the main reaction product is acetone. Methyl ethyl ketone and methyl vinyl ketone were not detected in the catalyzates from any of the three experiments. In experiments 2 and 3 the yield of acetone and acetaldehyde falls regularly. The catalyst was deactivated very quickly. During cleaning of the catalyst tube, a heavy carbonaceous deposit was found upon the catalyst. A similar observation is reported in the literature [6] for copper catalysts and attention is drawn to the favorable effect of hydrogen in the ketonization reaction. This role of additions of hydrogen is perceived in the scheme, which indicates that in the first instance vinyl ketones are formed and these are very susceptible to resinification and polymerization.

TABLE 1

Experiment No.	Temperature	Feed velocity of mixture (in ml/hour)	Products of reaction (in g)			
			Acetone	Methyl ethyl ketone	Acetaldehyde	Acetic acid
1	400°	15	21.6	–	1.6	–
2	460	15	13.0	–	0.8	–
3	440	25	3.5	–	–	Traces

Note: The amount of mixture in all experiments was 100 ml and the molar ratio of alcohol to anhydride was 1 : 1.

TABLE 2

Experiment No.	Temperature	Reaction products (in g)			
		Acetone	Methyl ethyl ketone	Acetaldehyde	Acetic acid
4	450°	6	1.1	–	–
5	435	10.2	3.2	–	–
6	420	28.0	6.0	–	–
7	405	14.0	5.2	0.8	Traces

Note: In all experiments the amount of mixture was 100 ml; the molar ratio of alcohol to anhydride was 1 : 1; the feed velocity of the mixture was 15 ml/hour.

The following experiments were carried out in presence of an equimolecular amount of hydrogen in relation to the alcohol. Results of experiments in presence of hydrogen are set forth in Table 2.

As we see from the data of Table 2, in experiments 4-7 the temperature was varied at constant molar ratio of components and constant space velocity. Maximum yield of methyl ethyl ketone was observed at 420°. The results of experiment 7 indicate that at low temperature a part of the acetic anhydride is hydrolyzed by water to acetic acid and does not enter into reaction.

The acetic acid in the reaction products was qualitatively detected by reaction with sodium carbonate and quantitatively determined by titration with caustic alkali solution. Acetaldehyde was identified through the semicarbazone (m.p. 162°). Characteristically the main product of the reaction was acetone, the amount of methyl ethyl ketone being 3 to 5 times smaller.

For establishment of the optimum conditions for formation of methyl ethyl ketone, in the following experiments the space velocity and molar ratio of components were successively changed. Results of these experiments are set forth in Table 3.

As we see from Table 3, the maximum feed velocity of the starting mixture was 40 ml/hour. The optimum molar ratio of components (ethanol and acetic anhydride) was 3 : 1.

Consequently the optimum conditions for methyl ethyl ketone formation are: temperature 420°; molar ratio of ethanol to anhydride 3 : 1; feed velocity of starting mixture of 40 ml/hour. The yield of methyl ethyl ketone was 27.5% of the theoretical calculated on the acetic anhydride. It should be noted that in the case of acetic acid and ethyl alcohol the yield of methyl ethyl ketone may reach over 90% [1].

2. Synthesis of methyl butyl ketones from butyl alcohol and acetic anhydride. All the experiments on synthesis of methyl butyl ketones were carried out in presence of hydrogen. The first experiment was carried out under the optimum conditions for formation of methyl ethyl ketone.

After fractionation of the catalyzate and elimination of water and unreacted butyl alcohol, two fractions were collected: 1st fraction with b.p. 116-118°; 2nd fraction with b.p. 126-129°.

In the first fraction was detected and identified methyl sec-butyl ketone:

B.p. 116-118° at 750 mm n_D^{20} 1.3998, d_4^{20} 0.812, MR_D 29.87, 2,4-dinitrophenylhydrazone m. p. 107°; a mixed test did not give a melting point depression; semicarbazone m. p. 106° (literature data: m. p. 108 and 106° respectively).

TABLE 3

Experiment No.	Molar ratio of components	Feed velocity of mixture (in ml/hour)	Products of reaction (in g)			
			Acetone	Methyl ethyl ketone	Acetaldehyde	Acetic acid
8	1 : 1	30	23.1	6.8	–	–
9	1 : 1	40	18.0	7.6	–	Traces
10	1 : 1	50	12.0	4.8	0.4	3.1
11	1 : 1	40	8.0	8.0	–	–
12	3 : 1	40	6.1	8.8	–	–
13	4 : 1	40	4.0	6.1	–	–

Note: Amount of mixture in all experiments 100 ml; temperature 420°.

TABLE 4

Experiment No.	Amount of mixture (in ml)	Molar ratio of alcohol to anhydride	Temperature	Products of reaction (in g)				
				Acetone	Methyl sec-butyl ketone	Methyl n-butyl ketone	Acetic acid	Butyraldehyde
2	75	3 : 1	435°	2.1	8.0	2.0	—	16.4
3	75	3 : 1	450	1.4	10.1	3.2	Traces	12.4
4	75	3 : 1	465	0.2	7.8	1.6	1.8	9.1
5	56.5	2 : 1	450	1.9	11.8	3.2	Traces	11.4

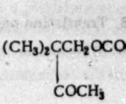
Note: Feed velocity of the mixture in all experiments 40 ml/hour.

A series of experiments was carried out to establish the optimum conditions for production of methyl butyl ketones. Results are set forth in Table 4.

The data of Table 4 show that the optimum conditions for catalytic synthesis of methyl butyl ketones are: molar ratio of butyl alcohol and acetic anhydride 2 : 1, space velocity 40 ml/hour, temperature 450°.

The yield of methyl sec-butyl ketone was 60% of the theoretical reckoned on the acetic anhydride; that of methyl n-butyl ketone was 16%.

3. Synthesis of methyl isobutyl ketone from acetic anhydride and isobutyl alcohol. Experiments were carried out in presence of hydrogen. The first experiment was performed under the optimum conditions for production of methyl butyl ketones; from the catalyzate was then isolated isobutyraldehyde with b.p. 64°, n_D^{20} 1.373, and methyl isobutyl ketone, b.p. 117° at 750 mm, n_D^{17} 1.3965, d_4^{17} 0.8038, MR_D 29.92, calculated 29.92; semicarbazone m.p. 132.0-132.0°, no depression in mixed test; 2,4-dinitrophenylhydrazone m.p. 94°.

According to the reaction scheme the formation of an ester with the structure  $(CH_3)_2\underset{\displaystyle COCH_3}{\underset{|}{C}}CH_2OCOCH_3$, is possible, but this ester was not found when the catalyzate was examined.

It is necessary to point out that the yield of methyl isobutyl ketone was insignificant and amounted to 3.2% of the theorectical reckoned on the acetic anhydride. The yield could not be improved by varying the various conditions of catalysis.

Analysis of the gases. Only those gases were examined which were obtained under optimum conditions for the respective ketones. The unsaturated hydrocarbons, carbon monoxide and carbon dioxide were investigated. Results of gas analysis are set forth in Table 5.

From the data of Table 5 we see that unsaturated hydrocarbons are only obtained when hydrogen is not additionally fed into the system. The yield of carbon dioxide is also characteristic: when the system contains additionally introduced hydrogen, the yield of CO_2 falls 4-5 times, while the yield of carbon monoxide increases. It may be assumed that in the instant of its formation the CO_2 is reduced to CO by hydrogen.

TABLE 5

Results of gas analysis

Number of experimental series		Composition of gas (in vol.-%)		
		Unsaturated hydrocarbons	Carbon monoxide	Carbon dioxide
1	Without hydrogen	4.5	11	8
	With hydrogen	–	17	1.5
2	Without hydrogen	5	21	13
	With hydrogen	–	29	3.5
3	Without hydrogen	–	19.5	1.0
	With hydrogen	5.4	18	4

SUMMARY

1. It was established that acetic anhydride and ethyl, n-butyl and isobutyl alcohols can serve as components of the ketonization reaction whose mechanism had been proposed by one of us.

2. A new method of synthesis of ketones was developed starting from acid anhydrides and alcohols.

3. The following were synthesized: a) methyl ethyl ketone from acetic anhydride and ethanol in a yield of 27% reckoned on the acetic anhydride; b) methyl sec-butyl ketone from acetic anhydride and butyl alcohol in a yield of 60% and methyl n-butyl ketone in a yield of 16% reckoned on the acetic anhydride; c) methyl isobutyl ketone from acetic anhydride and isobutyl alcohol in a yield of 3.2%.

4. It was established that only in presence of hydrogen is the catalytic synthesis of saturated ketones from alcohols and acid anhydrides possible.

5. The chrome-manganese catalyst does not deteriorate in presence of hydrogen and does not require regeneration.

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* T. p. = C. B. Translation pagination.

INFLUENCE OF THE ACIDITY OF THE MEDIUM ON THE COMPOSITION OF TARTRATE COMPLEXES OF COBALT

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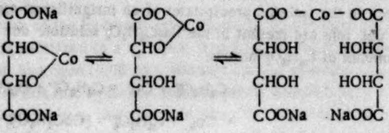
In an investigation of the tartrate complex of cobalt we established [1] that in presence of a complex peptizer (solution of tartrate and alkali) with a ratio of equivalents of $Na_2C_4H_4O_6$ and NaOH in the range of 1 : 1 to 2 : 1, the complex $Na_2[CoC_4H_2O_6]$ is formed. When studying the tartrate complex of bismuth, copper and cadmium, we satisfied ourselves that, depending on the concentration of tartrate and alkali, the composition of the complex changes. With increasing concentration of tartrate the formation of complexes proceeds at the expense of the carboxyl and hydroxyl groups of the tartrate.

Reaction of solutions of sodium tartrate with salts of cadmium and copper gives the complexes $Na_2[Me(C_4H_4O_6)_2]$, where Me = $Cd^{\cdot\cdot}$ or $Cu^{\cdot\cdot}$; consequently complex formation proceeds at the expense of the carboxyl groups [1]. Hence, by analogy, we may suggest that with falling pH of the solution the reaction of formation of tartrate complexes of cobalt ought to proceed according to the scheme:



(I) (II) (III)

(1)

On this basis we should expect that with falling concentration of NaOH in the complex peptizer, the formation of the complex ought to proceed at the expense of one carboxyl and one hydroxyl group of the tartrate, or only at the expense of its carboxyl groups. We decided that it was of interest to verify this hypothesis experimentally. The complex (II) was prepared from solutions with a ratio of equivalents of tartrate and caustic alkali in the range of 4 : 1 to 8 : 1. We determined the composition of the resultant complexes by the previously developed method, whose main features are outlined below.

The complex is precipitated by running 20-25 ml 96% alcohol into the solution. The precipitate is quickly filtered and washed with alcohol until free from OH' and SO_4'' ions. The wet precipitate is then transferred to a porcelain dish, dried to constant weight at 105° and analyzed.

A weighed amount of 0.18-0.2 g precipitate is carefully burned and ignited in a porcelain crucible (for determination of the content of volatiles). The solid is transferred to a beaker, treated with hot water, and left to stand; the solution is then filtered into a flask. This operation is repeated until the solution is neutral to phenolphthalein. After being made alkaline, the residue in the beaker is transferred to a filter. The amount of alkali in the filtrate is determined and recalculated for sodium.

The residue and filter are transferred to a beaker and dissolved with heating in 2 N sulfuric acid. Since the solid dissolves very slowly, a little concentrated sulfuric acid is added to the solution which is heated and then stood for 12 hours. The solution is then evaporated down and the cobalt is determined [2].

From the determination of the composition (we omit numerical data) it could be concluded that in the compounds formed the amount of sodium decreases while that of cobalt increases in comparison with the complex (I) for which was calculated(%): Na 18.3; Co 23.4. Thus, for example, when using a complex peptizer with an 8 : 1 ratio of equivalents the following contents were found: Na 11.61%; Co 24.55%. For the complex $Na[CoC_4H_3O_6]$ were calculated(%): Na 10.04; Co 25.74. From a comparison of these figures we can conclude that under these conditions equilibrium (1) is shifted in the direction of formation of the complex $Na[CoC_4H_3O_6]$. It was impossible to separate complex (II). Consequently with participation of a complex peptizer in the solution two complexes (I) and (II) are formed, but the relative amount of complex (II) increases with decreasing concentration of NaOH in the complex peptizer.

For the preparation of the complex $Na_2[Co(C_4H_4O_6)_2]$ (III), formed at the expense of only the carboxyl groups,

TABLE 1

Taken (in ml)		Weight of dry precipitate (in g)	0.1 N HCl used (ml)	Found (%)	
0.5 N $Na_2C_4H_4O_6$	0.5 N $Co(NO_3)_2$			Na	Co
25	5	0.2046	9.60	10.79	16.86
20	4	0.1980	9.05	10.51	16.95

TABLE 2

Taken (in ml)		Weight of dry precipitate (in g)	0.1 N HCl used (ml)	Found (%)	
0.5 N $Na_2C_4H_4O_6$	0.5 N $CoSO_4$			Na	Co
20	4	0.2024	10.05	11.42	11.62
20	4	0.2232	10.95	11.28	14.54

4-5 ml 0.5 N solution of $CoSO_4$ or $Co(No_3)_2$ was run into 20-25 ml 0.5 N solution of $Na_2C_4H_4O_6$. Analysis was performed as above. Results obtained are set forth in Table 1.

From an examination of the data of this table we see that complexes (III) and (II) are present in the compounds formed. Found %: Na 10.65; Co 16.90; $C_4H_4O_6''$ 72.45. $Na_2[Co(C_4H_4O_6)_2]$. Calculated %: Na 11.49; Co 14.70; $C_4H_4O_6''$ 73.81. The presence in the isolated precipitates of an insignificant amount of complex (II) is evidently to be explained by the fact that OH' ions are present in the $Na_2C_4H_4O_6$ solution. due to hydrolysis, and these make possible the formation of a small amount of $C_4H_3O_6'''$ anions:

$$C_4H_4O_6'' + OH' = C_4H_3O_6''' + H_2O,$$

$$Co'' + C_4H_3O_6''' = [CoC_4H_3O_6]' .$$

With the objective of completely suppressing the formation of $Na[CoC_4H_3O_6]$ and of obtaining solely $Na_2[Co(C_4H_4O_6)_2]$, we decided to lower the pH of the sodium tartrate solution; for this we carried out experiments using a solution of $Na_2C_4H_4O_6$ brought to acid reaction in presence of methyl red indicator (Table 2). The composition was determined by the previously described method with the following modification: the complex was brought down with 96° alcohol and washed with dilute 70° alcohol until free from SO_4''. The reason for the modification was that in presence of salts (obtained on neutralizing $Na_2C_4H_4O_6$)the addition of 96° alcohol brings down unreacted tartrate together with the complex ' The data of Table 2 show that the formula of the complex formed is $Na_2[Co(C_4H_4O_6)_2]$.

SUMMARY

1. The reaction of formation of tartrate complexes of cobalt in presence of a solution of a complex peptizer proceeds according to scheme (1). With decreasing concentration of the NaOH solution of the complex peptizer, the equilibrium is shifted from left to right in the equation $[CoC_4H_2O_6]' + H^{\cdot} \rightleftharpoons [CoC_4H_3O_6]'$.

2. Reaction of solutions of $Na_2C_4H_4O_6$(pH 4.4) with cobalt salts gives the tartrate complex $Na_2[Co(C_4H_4O_6)_2]$.

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STUDY OF THE REACTION OF TRIALKYSILANES WITH ALCOHOLS

SYNTHESIS OF TRIALKYLALKOXYSILANES AND THEIR PHYSICAL PROPERTIES

B.N. Dolgov, N.P. Kharitonov and M.G. Voronkov

One of the principal differences between the chemistry of silicon and the chemistry of carbon is the very much greater reactivity (which is also specific) of the Si – H bond in comparison with the C – H bond. Thus, for example, the Si – H bond is readily cleaved by water [1-8], alcohols [9-20], ammonia [21, 22, 25] and amines [21-24, 35] in presence of the suitable bases – hydroxides, alcoholates and amides of alkali metals – according to the general scheme:

$$\geqslant Si-H + HX \xrightarrow{MX} \geqslant Si-X + H_2$$

$$(X = OH,\ OR,\ NH_2,\ NHR,\ NR_2;\quad M = Li,\ Na,\ K).$$

The Si - H bond is also cleaved by water in presence of ammonia [25] or organic bases like piperidine [14, 26] or tetraalkylammonium hydroxides [27]. Cleavage of the Si - H bond also takes place under the action of alcoholic solutions of ammonia [15]. By contrast, the Si - H bond exhibits adequate stability towards dilute mineral acids and is completely inert to pure water and alcohols.

All these reactions of substitution of the hydrogen atom linked to silicon have no analogy in organic chemistry. They occur because the Si – H bond is polarized in a different direction to the C – H bond due to silicon possessing a lower electron affinity (0.60 eV) than hydrogen (0.76 eV), whereas carbon possesses an electron affinity (1.37 eV) greater than that of hydrogen. Due to this, the hydrogen atom bound to silicon carries a negative charge and is susceptible to cleavage in the form of hydride ion. All this indicates that, when drawing an analogy between the chemistry of silicon and the chemistry of carbon, we ought to compare the Si – H bond not with the C – H bond but with the similarly polarized carbon – halogen bond.

The present work is devoted to a study of the reaction of trialkylsilanes with alcohols. All the cited literature studies which report reactions at the Si – H bond were carried out solely with primary alcohols. In not one of these investigations was an attempt made to study the influence on the course of alkoxylations of the Si – H bond of the structure of the alcohol and of the nature of the alkaline catalyst. Only in an investigation by Price [9] was a study made of the influence on the speed of reaction of the Si – H bond with alcohols of the substituents at the silicon atom. In this investigation, however, the final products of reaction were not isolated.

We have shown that trialkalysilanes R_3SiH ($R = C_2H_5$, n-C_3H_7, n-C_4H_9) react with primary, secondary and tertiary alcohols in presence of alkoxides of alkali metals; in the case of primary and secondary alcohols the reaction is effected by simple boiling of the mixture of trialkylsilane and alkali metal solution (molar ratio of the latter to the original R_3SiH is 4-25%) in double the theoretical amount of the corresponding anhydrous alcohol. The yields of trialkylalkoxysilanes are lowered by the presence of water in the original alcohol or by the use of alcoholic solutions of hydroxides of alkali metals due to formation of products of hydrolysis – hexaalkyldisiloxanes. The progress of the reaction is readily followed from the volume of hydrogen formed, which is usually separated in the theoretical amount. The trialkylalkoxysilanes formed in the reaction whose yields are 80-90%, are separated by fractional distillation of the reaction mixture at the ordinary or reduced pressure.

In the absence of catalysts the trialkylsilanes do not react with alcohols. Thus, for example, on boiling triethylsilane with anhydrous ethyl alcohol in a quartz vessel in the course of 24 hours, no reaction whatever was observed.

The experimental data obtained in the present work permit us to recognize the following regularities in the reaction of trialkylsilanes with alcohols.

The velocity of reaction of trialkylsilanes with alcohols decreases with increasing length of the alkyl radicals R in R_3SiH. Thus, for instance, the theoretical amount of hydrogen in the reaction of n-butyl alcohol in presence of 8-mole-% C_4H_9ONa with triethylsilane comes off after 4 hours, with tri-n-propylsilane after 5 hours, and with tri-n-butylsilane after 10 hours.

With increasing length of the alcoholic radical the speed of reaction of trialkylsilanes with primary normal alcohols is slightly lowered. Owing to the considerable steric hinderance, isobutyl alcohol reacts with triethylsilane more slowly than isoamyl alcohol, while the latter reacts with the same velocity as normal alcohols.

A profound influence upon the reaction of trialkylsilanes with alcohols is exerted by the nature of the alkali metal alkoxides. With increasing atomic number of the alkali metal (from lithium to rubidium), the velocity of reaction of trialkylsilanes with alcohols rises, while the yields of the resultant trialkylalkoxysilanes fall. Increased concentration of alkoxide in the reaction mixture leads to a certain increase in the reaction velocity andin the yields of trialkylalkoxysilanes. In addition the nature of the alkali metal alkoxide affects the reaction of trialkysilanes with alcohols at normal pressure in the following manner. In presence of lithium alkoxides trialkylsilanes react only with primary alcohols. In presence of sodium alkoxides trialkylsilanes react not only with primary but also with secondary alcohols. In the latter case, however, the reaction often proceeds slowly and doesmot proceed to the end, while the yields of trialkyl-sec-alkoxysilanes are relatively low. When using potassium alkoxides as catalysts, trialkysilanes react substantially equally well with primary and secondary alcohols. Tertiary alcohols and phenols do not react with trialkylsilanes in presence of thecorresponding alkoxides of lithium, sodium and potassium. Mercaptans likewise do not react with trialkylsilanes in presence of mercaptides of alkali metals. In presence, however, of alkoxides of rubidium, trialkylsilanes also react with tertiary alcohols. It must be admitted that in the latter case the reaction does not proceed to the end, and the yield of trialkyl-tert-alkoxysilanes is low (of the order of 10%).

When the reaction is performed in an autoclave at 200-210° in presence of the corresponding sodium alkoxides, the trialkylsilanes smoothly react not only with primary and secondary but also with tertiary alcohols. In this way we synthesized a series of trialkyl-tert-alkoxysilanes in a yield of 80-85%. The synthesis of these compounds is especially interesting since it is difficult to prepare trialkyl-tert-alkoxysilanes by the usual methods. In particular we failed in an attempt to obtain triethyl-tert-butoxysilane by transesterification of triethylmethoxysilane with tert-butyl alcohol in presence of sodium tert-butoxide.

On the other hand the transesterification of triethylmethoxysilane with n-butyl and isobutyl alcohols in presence of the corresponding sodium butoxides permitted us to obtain the n-butoxy and isobutoxy derivatives in 80-90% yield. Transesterification of triethylmethoxysilane with sec-butyl alcohol proceeds slowly, due to which the yield of triethyl-sec-butoxysilane is low.

We also found that triethylsilane reacts with ethyl alcohol also in the absence of an alkaline catalyst when the reaction is carried out in an autoclave at 200°, triethylethoxysilane being formed in a yield of 88%. We think it probable, however, that in this case metallic copper or iron were catalysts of the reaction, since at the end of the reaction the copper obturator and the walls of the autoclave were found to be corroded. This inference is also supported by the fact that triethylsilane reacts with ethyl alcohol in presence of active copper powder on boiling at the oridinary pressure. In this case, however, the yield of triethylethoxysilane is low (11%) and the reaction proceeds slowly.

The reaction of trialkylsilanes with alcohols (and water) which is catalyzed by alkoxides of alkali metals is undoubtedly an ionic one. This is confirmed by the fact that in the absence of alcohols the individual alkoxides (and also the anhydrous hydroxides) of alkali metals do not react with trialkylsilanes. Our experimental data conclusively prove that the reaction of trialkylsilanes with alcohols is a bimolecular nucleophilic substitution (S_n 2, according to Ingold and Hughes) whose mechanism may be represented by the following scheme;

$$R'O^- + R_3SiH \longrightarrow [R'O \ldots R_3Si \ldots H]^- \xrightarrow{+R'OH} R'OSiR_3 + H_2 + R'O^- .$$

This scheme shows that the attack of the electron-donating alkoxyl ion on the positively polarized silicon atom leads to cleavage of the hydride ion which quickly combines with the alcohol with liberation of a molecule of hydrogen. The latter stage leads to liberation of the alkoxyl ion. The above scheme explains themechanism of the catalytic action of alkali metal alkoxides which bring about an increase in the concentration of basic OR^-.

It is most probable that entering into the composition of the complex $[R'O \ldots R_3Si \ldots H]^-$, formation of which is hindered by H^+ ions, are a molecule of alcohol together with the alkoxyl ion, so that both of the above-indicated stages proceed simultaneously.

Consequently the reaction velocity, depending on the concentration of OR^- ions (and on the lengths of ions $R'OH_2^+$), is determined by the dissociation constant and by the concentration of alkoxide of the alkali metal and by the autoprotolysis constant of the alcohol.

Increase in the size of the alkyl radicals in the trialkylsilanes, leading to a fall in the velocity of their reaction with alcohols, creates a stronger field of force, due to which the energy barrier for penetration of the alkoxyl ions to the silicon atom becomes larger, whereas the stability of the Si–H bond remains substantially unchanged with increasing size of the alkyl radicals in trialkylsilanes. This is confirmed by infrared spectroscopic data obtained in the present investigation which show that the absorption band corresponding to the valence vibration of Si–H in three trialkylsilanes R_3SiH ($R = C_2H_5$, $n\text{-}C_3H_7$ and $n\text{-}C_4H_9$) is identical (2106 ± 2 cm^{-1})*. This frequency of the Si–H bond in trialkylsilanes is smaller than in trichlorosilane (2257 cm^{-1}) and in tribromosilane (2236 cm^{-1}),** which reflects the lower

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* In the literature are given the vibration frequency of Si–H in trimethylsilane [28] and methyldiallylsilane [29] determined by Raman spectrography; the respective values are 2118 and 2117 cm^{-1}.

** Data for tribromosilane were obtained by Raman spectrography [30].

TABLE 1

Autoprotolytic constant (pK) of compounds containing a mobile hydrogen at 25° [32]

Formula	pK	Formula	pK
H_2SO_4	3.0	CH_3OH	16.7
HCOOH	6.3	C_2H_5OH	19.0
CH_3COOH	12.6	NH_3	22 (−34°)
HOH	14.0		

stability of the Si−H bond in trialkylsilanes (due to the influence of the halogen atoms, the polarization of the Si−H bond in trihalogenosilanes, and consequently also their susceptibility to reactions of nucleophilic substitution, is sharply reduced).

The sharp drop in velocities of reactions of trialkylsilanes with alcohols on passing from primary to secondary and, in particular, to tertiary alcohols, as also the small decrease of reaction velocities with increasing length of the alcohol radical or on passing from normal to iso alcohols, are accounted for by the same steric hindrances to nucleophilic attack of the silicon atom by the alkoxyl ion (particularly if it is solvated). These steric hindrances, associated with increasing branching of the alcoholic radical, evidently are many times greater than the accompanying increase of basicity of the alcohol (due to the inductive effect of the alkyl groups) which promotes the alkoxylation of trialkylsilanes.

Alcohols which do not contain sterically-hindering radicals but which possess acidic properties (phenols), as well as water, organic acids [36] and mercaptides, do not react with trialkylsilanes. Thus, for example, we failed to observe a reaction of triethylsilane with phenol when boiled in presence of phenates of lithium, sodium or potassium. Similarly no reaction occurred between triethylsilane and organic acids in presence of their alkali metal salts.

Triethylsilane is completely unchanged after prolonged boiling with water or with 1 N aqueous NaOH and KOH, in which it is insoluble. Furthermore, the reaction of triethylsilane with aqueous solutions of NaOH or KOH does not proceed even in a homogeneous medium obtained by addition of dioxane (but not of alcohol). Such a difference in reactivity of trialkylsilanes with alcohols on the one hand and with water, phenols, mercaptans and organic acids on the other is explained by the higher autoprotolytic constant of alcohols in comparison with water, phenols, mercaptans and carboxylic acids (see Table 1). As further evidence in support of this conclusion, methyl alcohol, which possesses a lower autoprotolytic constant than ethyl alcohol, differs from the latter in not reacting with silane in presence of lithium alkoxide [31]. Ammonia, possessing a very high autoprotolytic constant, on the contrary reacts with triethylsilane in presence of potassium amide even at −35° [35].

The influence of the nature of the cation in the alkali metal alkoxide catalyzing the reaction of trialkylsilanes with alcohols is associated with the rise in atomic number of the metal, i.e., in passing from lithium to rubidium there is a considerable rise in the degree of ionization (alkalinity), leading to a rise in the concentration of alkoxyl ions and, consequently, to a rise in reaction velocity.

All the foregoing considerations indicate that reactions of trialkylsilanes with alcohols and other compounds containing mobile hydrogens (water, ammonia, amines), which proceed according to the S_N2 type, are promoted by the fall of concentration of H^+-ions which takes place with rise of the autoprotolytic constant of the reactant (solvent) and with rise of concentration of negative ions ($R'O^-$ in the case of alcohols) and which is intensified with increasing atomic number of the alkali metal whose derivative serves as the catalyst.

In the course of the present investigation we synthesized 28 pure trialkylalkoxysilanes and determined their physical properties, which are set forth in Table 2; 27 of these compounds have not previously been reported in the literature. Triethylphenoxysilane was prepared by reaction of triethylsilane with phenol in presence of iodine and aluminum iodide by the method which we developed for synthesis of trialkylacyloxysilanes [36].

The reaction of trialkylsilanes with alcohols studied by us is a convenient general method of alkoxylation of the Si−H bond. This method is distinguished by its simplicity and by the high yields of alkoxy derivatives, which are easily separated in the pure form owing to the absence of any secondary reaction products.

EXPERIMENTAL

Starting components

Trichlorosilane was obtained in a yield of about 75% by the reaction of hydrogen chloride with silicon or with high-percentage ferrosilicon at 290-300°. The $HSiCl_3$ purified in a column had b.p. 31.8° (760 mm).

Triethylsilane, tri-n-propylsilane and tri-n-butylsilane were prepared by reaction of the corresponding alkyl magnesium chlorides with trichlorosilane and purified by distillation in a column (tributylsilane was distilled in vacuum). Their yields, physical properties and analyses are set forth in Table 3.

The starting alcohols were purified by distillation in a column and possessed constants identical with the best literature data [33]. Alcohols with b.p. below 100° were previously freed from water by boiling with metallic calcium. Tert-butyl alcohol was repeatedly frozen after distillation.

TABLE 2

Trialkylalkoxysilanes R_3SiOR'

Trialkylalkoxy silane No.	R_3SiOR'	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$	γ^{20}
1	$(C_2H_5)_3SiOCH_3$	141.5°	760	0.8203	1.4129	0.0081	21.63
2	$(C_2H_5)_3SiOC_2H_5$	154.0	760	0.8160	1.4140	0.0082	22.09
3	$(C_2H_5)_3SiOCH_2CH_2CH_3$	175.3	760	0.8159	1.4177	0.0076	22.88
4	$(C_2H_5)_3SiOCH(CH_3)_2$	166.5	760	0.8079	1.4133	0.0083	20.84
5	$(C_2H_5)SiOCH_2CH_2CH_2CH_3$	193.8	760	0.8186	1.4210	0.0074	23.00
6	$(C_2H_5)_3SiOCH_2CH(CH_3)_2$	186.3	760	0.8129	1.4184	0.0084	22.35
7	$(C_2H_5)_3SiOCH(CH_3)CH_2CH_3$	187.0	760	0.8188	1.4203	0.0076	22.66
8	$(C_2H_5)_3SiOC(CH_3)_3$	178.5	760	0.8115	1.4181	0.0077	21.34
9	$(C_2H_5)_3SiOCH_2(CH_2)_3CH_3$	213.8	760	0.8212	1.4250	0.0083	23.46
10	$(C_2H_5)_3SiOCH_2CH_2CH(CH_3)_2$	205.7	760	0.8176	1.4237	0.0072	23.25
11	$(C_2H_5)_3SiOC(CH_3)_2C_2H_5$	201.2	760	0.8253	1.4270	0.0075	23.25
12	$(C_2H_5)_3SiOCH_2)CH_2)_4CH_3$	231.3	760	0.8230	1.4281	0.0081	25.23
13	$(C_2H_5)_3SiOCH_2(CH_2)_5CH_3$	248.0	760	0.8255	1.4310	0.0080	24.99
14	$(C_2H_5)_3SiOCH_2(CH_2)_6CH_3$	267.0	760	0.8267	1.4332	0.0076	25.40
15 *	$(C_2H_5)_3SiOCH_3{}'CH_3)(CH_2)_6CH_3$?	256.3	760	0.8259	1.4327	0.0075	25.50
16	$(C_2H_5)_3SiOC_6H_{11}$	237.1	760	0.8769	1.4481	0.0080	27.12
17	$(C_2H_5)_3SiOC_6H_5$	243.6	760	0.9304	1.4880	0.0134	29.66
18	$(C_2H_5)_3SiOCH_2C_6H_5$	262.6	760	0.9319	1.4852	0.0125	28.64
19	$(C_2H_5)_3SiOCH_2CH_2OC_2H_5$	210.9	760	0.8650	1.4237	0.0080	25.06
20	$(C_2H_5)_3SiOCH_2CH_2NH_2$	201.6	760	0.8749	1.4385	0.0082	26.94
21	$(n.C_3H_7)_3SiOCH_2(CH_2)_2CH_3$	102.5	9	0.8203	1.4300	0.0075	24.66
22	$(n.C_3H_7)_3SiOCH_2CH(CH_3)_2$	90.5	5	0.8140	1.4280	0.0077	23.59
23	$(n.C_3H_7)_3SiOCH\ CH_3)C_2H_5$	91.5	6.5	0.8204	1.4289	0.0079	24.11
24	$(n\text{-}C_3H_7)_3SiOC(CH_3)_3$	84.5-85.0	6	0.8151	1.4280	0.0075	23.48
25	$(n.C_4H_9)SiOCH_2(CH_2)_2CH_3$	123.5-124.0	5	0.8285	1.4370	0.0078	25.44
26	$(n.C_4H_9)_3SiOCH_2CH(CH_3)_2$	121.0	6	0.8220	1.4351	0.0075	24.27
27	$(n.C_4H_9)_3SiOCH(CH_3)C_2H_5$	130.0	9	0.8229	1.4362	0.0076	25.30
28	$(n.C_4H_9)_3SiOC(CH_3)_3$	120.5	7	0.8199	1.4350	0.0081	24.89

* Subscripts in formula illegible in original.

TABLE 3

Properties of Trilkylsilanes R_3SiH

R_3SiH	Yield (in % of theoretical)	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$	γ^{20}	Molecular wt.		Si (in %)	
								Calculated	Found	Calculated	Found
$(C_2H_5)_3SiH$	70	107.7°	760	0.7309	1.4121	0.0081	20.52	116.28	113.4	24.14	24.00
$(iso.\text{-}C_3H_7)_3SiH$	66.7	173.2	760	0.7580	1.4272	0.0082	22.98	158.36	157.4	17.72	17.62
$(iso.\text{-}C_4H_9)_3SiH$	65.1	88-89	5	0.7795	1.4380	0.0083	24.86	200.43	199.0	14.00	13.85

The metallic lithium, sodium, potassium and rubidium were the commercially pure preparations.

EXPERIMENTAL PROCEDURE

All the reactions of trialkylsilanes with alcohols at the ordinary pressure were carried out in two-necked, round-bottomed flasks with a volume of 100 ml, equipped with reflux condenser and thermometer. The top end of the condenser was joined to a gasholder for collection of hydrogen through a Tishchenko bottle filled with concentrated sulfuric acid. Reactions under pressure were carried out in a 225 ml steel autoclave.

Syntheses were effected by heating a mixture of 0.1 mole trialkylsilane with twice the theoretical amount of alcohol in which had previously been dissolved 0.1-1 g of the particular alkali metal. Heating was continued until hydrogen ceased to come off. The excess of alcohol and the trialkylalkoxysilane formed were dissolved off

TABLE 2 Continued

Molecular weight		Analysis (in %)						Yield of R_3SiOR' (in %) in presence of		
		C		H		Si				
Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	LiOR'	NaOR'	KOR'
146.30	145.6, 144.2	57.48	56.99, 56.94	12.34	12.36, 12.30	19.19	19.01, 19.03	–	92.7	93.0
160.33	160.0, 158.4	59.94	59.77, 59.73	12.58	12.60, 12.58	17.50	17.30, 17.38	46.8	83.0	90.1
174.36	173.4, 172.3	62.04	61.79, 61.81	12.72	12.86, 12.74	16.10	15.92, 16.01	–	83.0	–
174.36	172.9, 171.3	62.04	61.93, 62.04	12.72	12.89, 12.72	16.10	15.91, 16.00	0	14.3	80.0
188.38	187.7, 185.9	63.76	63.54, 63.63	12.84	12.82, 12.99	14.88	14.71, 14.71	–	85.6	–
188.38	188.1, 186.4	63.76	63.49, 63.50	12.84	12.93, 12.92	14.88	14.69, 14.81	–	81.3	–
188.38	188.2, 186.1	63.76	63.61, 63.19	12.84	12.99, 12.86	14.88	14.68, 14.79	0	8.0	90.3
188.38	186.3, 185.4	63.76	–	12.84	–	14.88	14.68, 14.69	0	0; 84.0*	0**
202.41	200.2, 199.1	65.39	64.77, 64.99	12.96	13.00, 13.09	13.87	13.60, 13.68	–	86.8	–
202.41	201.3, 201.6	65.39	65.07, 65.09	12.96	13.00, 13.12	13.87	13.66, 13.77	–	81.4	–
202.41	199.0, 198.6	65.39	–	12.96	–	13.87	13.62, 13.69	0	0; 85.4*	0
216.43	215.4, 211.4	66.59	65.98, 66.19	13.04	13.10, 13.00	12.97	12.81, 12.73	–	88.9	–
230.46	228.8, 227.1	67.75	67.50, 67.28	13.12	13.28, 13.19	12.18	11.88, 11.99	–	91.4	–
244.49	244.2, 243.8	68.35	67.85, 67.88	13.19	13.30, 13.21	11.47	11.31, 11.43	–	81.0	–
244.49	242.8, 241.9	68.35	67.95, 67.91	13.19	13.20, 13.26	11.47	11.27, 11.32	0	–	80.5
214.42	214.1, 213.6	67.22	66.79, 66.84	12.22	12.30, 12.30	13.08	12.92, 12.97	0	–	81.0
208.37	206.4, 206.4	69.16	68.73, 68.88	9.67	9.79, 9.79	13.47	13.26, 13.29	0	0	0***
222.40	221.3, 222.7	70.21	69.85, 70.01	9.97	9.96, 10.01	12.61	12.40, 12.52	–	80.9	–
204.38	200.8 201.7	53.87	–	11.84	–	13.73	13.60, 13.69	–	92.3	–
175.35	172.0, 172.8	54.82	–	12.07	–	16.00	15.82, 15.87	–	84.9	–
230.46	229.1	67.75	–	13.12	–	12.18	11.99, 12.03	–	87.7	–
230.46	228.5	67.75	–	13.12	–	12.18	11.99, 12.01	–	85.4	–
230.46	226.9	67.75	–	13.12	–	12.18	11.94, 12.02	–	79.9	–
230.46	229.7	67.75	–	13.12	–	12.18	11.98, 11.99	–	82.5*	–
272.54	270.6	70.51	–	13.31	–	10.29	10.05, 10.17	–	87.6	–
272.54	269.2	70.51	–	13.31	–	10.29	10.09, 10.11	–	84.6	–
272.54	270.6	70.51	–	13.31	–	10.29	10.05, 10.05	–	80.8	–
272.54	272.0	70.51	–	13.31	–	10.29	10.09, 10.13	–	80.0*	–

* In autoclave at 210°. ** 6.8% in presence of $RbOC(CH_3)_3$. *** In presence of AlI_3. Yield 80.8%.

from the metal alkoxide, after which the trialkylalkoxysilane was purified by distillation in a column with an efficiency of 10-12 theoretical plates.

The method of determination of the physical constants and the accuracy of their determination are described in one of our papers [34]. For determination of the constants, all the substances were redistilled in a column, the middle cuts with constant boiling points being collected.

The infrared spectra of the trialkylsilanes were plotted in the region of the principal frequency of the Si – H vibration in a Perkin-Elmer 12B spectrophotometer fitted with a LiF prism. The spectral width of the slit was of the order of 3 cm^{-1}. The thickness of the layer was of the order of 0.007 mm. Electrooptical intensification.*

Silicon was determined by mineralization of the sample to SiO_2 with a mixture of oleum and fuming nitric acid [34]. Carbon and hydrogen were determined by combustion in a tube over copper oxide in presence of a mixture of lead acetate and potassium dichromate. The silica fume in the combustion tube was trapped by a plug of calcined asbestos inserted in the tube.

Below we give details of some of the more typical experiments.

Synthesis of triethylmethoxysilane. 31.8 g triethylsilane was added to a solution of 0.1 g sodium in 19.2 g methanol. The reaction mixture was boiled until hydrogen had entirely ceased to come off (4.5 hours); the amount of hydrogen was 8 liters. The reaction product was distilled off from the sodium methoxide and distilled in a column. Yield of triethylmethoxysilane with b.p. 141.4-141.8° (759 mm) 40.7 g (92.7%).

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* The infrared spectra were plotted by M.O. Bulanin, to whom the authors express their gratitude.

Synthesis of triethylethoxysilane.* a) To a solution of 0.1 g potassium in 9.2 g ethyl alcohol was added 11.6 g triethylsilane. The reaction starts even in the cold (hydrogen evolution). After 2 hours' heating of the reaction mixture at the boil, 2.3 liters hydrogen had come off. After distillation from the potassium ethoxide, the reaction product was distilled in a column. Yield of triethylethoxysilane with b.p. 153.0-153.7° (751 mm) 14.5 g (90.1%).

b) 11.6 g triethylsilane and 20.0 g ethyl alcohol were heated in an autoclave at 200° for 20 hours. After this period the pressure in the autoclave had reached 27 atm. After cooling the autoclave to room temperature, the internal pressure remained at 8 atm. The volume of hydrogen evolved during the reaction and passing into the gasholder was 2.2 liters. After the reaction had been carried out, the steel walls of the autoclave and the copper obturator were found to be corroded. Distillation of the reaction mixture in a column gave 14.0 g triethylethoxysilane with b.p. 152.0-153.6° (751.3 mm), i.e.,87.5% of the theoretical yield.

c) A mixture of 11.6 g triethylsilane, 9.2 g 96% ethyl alcohol and 1.5 g NaOH was heated to the boil for 3 hours. After this period 1.5 liters hydrogen had come off. Distillation of the reaction mixture in a column gave 6.4 g (40%) of triethylethoxysilane with b.p. 152.5-154.0°.

d) A mixture of 11.6 g triethylsilane and 9.2 g ethyl alcohol was boiled for 24 hours in a quartz flask. Evolution of hydrogen was not observed and the weight of triethylsilane remained unchanged.

e) A mixture of 11.6 g triethylsilane and 9.2 g ethyl alcohol was boiled in a quartz flask for 18 hours in presence of 1.75 g active copper powder. During this period 0.25 liter hydrogen was evolved. Distillation of the reaction mixture in a column gave 1.6 g triethylethoxysilane with b.p. 153.5-153.9° (747.6 mm). Treatment of the lower boiling fractions with water gave 8.3 g unchanged triethylsilane with b.p. 107.9-108.2° (747.6 mm).

Reaction of triethylsilane with water and aqueous alkalies

On boiling 11.6 g triethylsilane with 15 ml distilled water or with 15 ml 1 N KOH or NaOH for 24 hours, no reaction at all was observed. All the triethylsilane remained unchanged. On boiling a homogeneous mixture of 11.6 g triethylsilane, 3.6 g distilled water and 10 ml dioxane in which was dissolved 0.1 g metallic sodium, no evolution of hydrogen was observed in the course of 17 hours.** After treatment of the reaction mixture with water, 10.2 g unchanged triethylsilane was isolated. A similar result was obtained on replacing the sodium by 0.2 g metallic potassium.

Synthesis of triethylisopropoxysilane. To a solution of 1.0 g potassium in 12.0 g isopropyl alcohol was added 11.6 g triethylsilane. The mixture was heated at the boil for 3 hours, during which period 2.3 liters hydrogen came off. After distilling off from potassium isopropoxide, the reaction mixture was distilled in a column to give 14.0 g (80%) triethylisopropoxysilane with b.p. 166.5-167.0° (769.2 mm). A reduction in the amount of potassium leads to a fall in yield of triethylisopropoxysilane.

Reaction of 11.6 g triethylsilane with a solution of 0.8 g Na in 12.0 g isopropyl alcohol at the boil for 5 hours led to release of only 0.2 liter hydrogen. The yield of triethylisopropoxysilane was 2.5 g (14.3%). The greater part (10.0 g) of the triethylsilane did not enter into reaction and remained unchanged. When the reaction was carried out with a smaller amount of sodium (0.1 g), no triethylisopropoxysilane was formed under the conditions mentioned, and the whole of the triethylsilane remained unchanged.

On prolonged boiling of 11.6 g triethylsilane with a solution of 0.2 g lithium in 12.6 g isopropyl alcohol, no hydrogen was evolved and no triethylisopropoxysilane was formed. The whole of the original triethylsilane remained unchanged.

Synthesis of triethylisobutoxysilane. To a solution of 0.3 g sodium in 14.8 g isobutyl alcohol was added 11.6 g triethylsilane. After 2 hours' heating of the reaction mixture at the boil, the evolution of hydrogen ceased (its volume was then 1 liter). On adding a further 0.5 g sodium to the reaction mixture and continuing heating for 3 hours, a further 1.3 liters hydrogen came off (making 2.3 liters in all). Distillation in a column gave 15.2 g (81.3%) triethylisobutoxysilane with b.p. 184.5-186.0° (754.2 mm).

Synthesis of triethyl-tert-butoxysilane. A solution of 0.1 g sodium in 14.8 g tert-butyl alcohol and 11.6 g triethylsilane were heated in an autoclave at 200-205° for 20 hours. The maximum pressure was 25 atm. at 200° and 5 atm. at room temperature.

The evolved hydrogen occupied a volume of 2.3 liters when transferred to the gasholder. Distillation of the

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[*] When studying the reactions of triethylsilane with ethyl alcohol, we found that these two substances form a constant boiling mixture with b.p. 73.0-74.0° containing about 50% triethylsilane.

[**] An alcoholic solution of C_2H_5ONa by contrast smoothly reacts with triethylsilane in presence of an equal volume of dioxane.

reaction mixture gave 15.8 g triethyl-tert-butoxysilane with b.p. 176.7-178.2° (754.6 mm). No hydrogen evolution was observed on prolonged heating of triethylsilane with solutions of sodium or potassium in tert-butyl alcohol at atmospheric pressure, and the whole of the triethylsilane remained unchanged. Boiling for 8 hours of 11.6 g triethylsilane with a solution of 1.0 g rubidium in 14.8 g tert-butyl alcohol led to evolution of 0.15 liter hydrogen. The yield of triethyl-tert-butoxysilane with b.p. 177.2-178.4° (762.1 mm) and n_D^{20} 1.4180 was 1.3 g (6.8%). Reaction of triethylsilane with tert-butyl alcohol in presence of aluminum iodide is accompanied by release of hydrogen but leads to formation of hexaethyldisiloxane.

Synthesis of triethyl-n-heptoxysilane. To a solution of 0.3 g sodium in 23.2 g n-heptyl alcohol was added 11.6 g triethylsilane. The reaction mixture was heated at the boil for 3 hours. During this period 2.3 liters hydrogen was given off. Yield of triethyl-n-heptoxysilane with b.p. 247.3-247.6° (752.0 mm), 21.2 g (91.4%).

Synthesis of triethylcyclohexoxysilane. 11.6 g triethylsilane and a solution of 0.2 g potassium in 20.0 g cyclohexanol were boiled for 2 hours. During this period 2.2 liters hydrogen came off. After distilling off the reaction product from the alkoxide, the product was distilled in a column to give 19.2 g (81.0%) triethylcyclohexoxysilane with b.p. 236.9° (756.0 mm).

Synthesis of triethylbenzyloxysilane. A solution of 0.3 g Na [illegible] 14.1 g benzyl alcohol and 11.6 g triethylsilane were heated at the boil for 2 hours; during this period 2.4 liters hydrogen came off. The reaction mixture was distilled at first in vacuum and later in a column. Yield of triethylbenzoxysilane with b.p. 262.2-263.0° (764.2 mm) was 19 g (80.9%).

Synthesis of triethyl-β-aminoethoxysilane. On heating for an hour 11.6 g triethylsilane with a solution of 0.1 g sodium in 12.2 g ethanolamine, 2.4 liters hydrogen came off. The reaction mixture consisted of two layers (lower one of solution of alkoxide in ethanolamine, upper one of triethyl-β-aminoethoxysilane). Distillation of the upper layer in a column gave 14.9 g (84.9%) triethyl-β-aminoethoxysilane with b.p. 201.7° (761.9 mm).

Synthesis of tri-n-propylisobutoxysilane. To a solution of 0.2 g sodium in 14.8 g isobutyl alcohol was added 15.9 g tri-n-propylsilane. Boiling of the reaction mixture for 11 hours led to evolution of 2.3 liters hydrogen. Two distillations of the reaction mixture in vacuum gave 19.7 g (85.4%) tri-n-propylisobutoxysilane with b.p. 90.5° (5 mm).

Synthesis of tri-n-butyl-tert-butoxysilane. 20.1 g tri-n-butylsilane and a solution of 0.2 g sodium in 14.8 g tert-butyl alcohol were heated in an autoclave at 200-210° for 19 hours. The maximum pressure in the autoclave was 23 atm. During the reaction 2.3 liters hydrogen came off and was collected. After distilling off the excess of alcohol, the reaction mixture was distilled in vacuum to give 10.9 g (80%) tri-n-butyl-tert-butoxysilane with b.p. 120.5° (7 mm).

Synthesis of triethylphenoxysilane. To 18.8 g melted phenol was added 0.1 g aluminum powder and 1.5 g iodine, followed, with stirring, by 11.6 g triethylsilane. Heating of the reaction mixture at the boil for an hour caused 2.5 liters hydrogen to come off. Two distillations of the reaction mixture gave 16.7 g (80.3%) triethylphenoxysilane with b.p. 243.8° (762.8 mm).

Reaction of triethylsilane with sodium methoxide. 2.3 g sodium was dissolved while cooling in 6.4 g methanol. The alcohol was driven off in vacuum in an atmosphere of dry hydrogen, and the residual alkoxide was heated in a hydrogen stream on a water bath for a further 1.5 hours. To the so-prepared sodium methoxide was added 11.6 g triethylsilane. No hydrogen was evolved on boiling this mixture for 3 hours, and all the triethylsilane remained unchanged. A similar result was obtained on prolonged heating of triethylsilane with sodium methoxide in a medium of inert solvent (benzene).

Transesterification of triethylmethoxysilane with butyl alcohols. 14.6 g triethylmethoxysilane, 14.8 g n-butyl alcohol and 0.1 g sodium were slowly distilled in a column. 3.1 g methanol came over at 64.4-66.2° (760.2 mm). Further distillation gave 8.3 g excess n-butyl alcohol with b.p. 115.2-117.3° and 17.0 g triethyl-n-butoxysilane with b.p. 193.0-193.8° (760.2 mm). Yield 90.4% of the theoretical. After redistillation it had:

B.p. 193.8° (760.2 mm), n_D^{20} 1.4210, d_4^{20} 0.8185.
Found %: Si 14.66, 14.70. $C_{10}H_{24}OSi$. Calculated %: Si 14.88.

Transesterification of triethylmethoxysilane with isobutyl alcohol in completely identical conditions gave 14.6 g (77.4%) triethylisobutoxysilane with b.p. 185.9° (755.3 mm).

Found %: Si 14.79, 14.66. $C_{10}H_{24}OSi$. Calculated %: Si 14.88.

Transesterification of triethylmethoxysilane in similar conditions with sec-butyl alcohol leads to formation of only 3-5% triethyl-sec-butoxysilane with b.p. 186-188°, n_D^{20} 1.4203. The greater part of the triethylmethoxysilane remains unchanged.

An attempt to transesterify triethylmethoxysilane with tert-butyl alcohol failed. All the original triethylmethoxysilane was recovered unchanged.

SUMMARY

A study was made of the reaction of n-trialkysilanes R_3SiH ($R = C_2H_5$, n-C_3H_7, n-C_4H_9) with alcohols of various structures in presence of alkoxides of lithium, sodium, potassium and rubidium. A dependence was found of the course of this reaction on the structure of the trialkylsilane and alcohol and on the atomic number of the metal in the alkoxide used as catalyst. A mechanism is proposed for the reaction. It is shown that the reaction of trialkylsilanes with alcohols is a simple and convenient method of synthesis of trialkylalkoxysilanes, which are formed in yields of 80-90% of the theoretical. Syntheses were effected of 28 (27 for the first time) trialkylalkoxysilanes, and their physical properties were determined.

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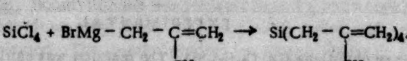
SYNTHESIS OF TETRAISOBUTYL-, TETRAISOPROPYL-, TETRACYCLOHEXYL- AND TETRA-α-NAPHTHYLSILANES

A.D. Petrov and T.I. Chernysheva

On carrying out the condensation according to the scheme $R_3CX + RMgX \rightarrow R_4C + MgX_2$ at elevated temperature or in presence of $HgCl_2$, Petrov and Chernyshev [1] obtained tetra-n-propyl and tetra-n-butylmethanes in low yields and showed that the synthesis of tetra-n-hexylmethane cannot be realized at all due to the facility of cleavage of HCl from trihexylchloromethane. The synthesis of tetraalkylsilanes, by analogous scheme, takes place with high yields even when using high-molecular alkyl halides [2], both owing to the greater ionization of the $\rightarrow Si - X$ bond and owing to the inability of trialkylhalosilanes to cleave off HX. However, in spite of this, and also of the lower steric hindrance in the synthesis of silanes due to the higher atomic radius of silicon., only triisobutylsilane has been prepared by the action of isobutylsodium on $SiCl_4$ (probably because the fourth atom of chlorine was substituted not by the isobutyl radical but by sodium) [3]. Introduction into the isobutyl radical of a double bond in the beta-position enabled Petrov and Nikishin [4] to overcome the steric hindrances here arising and to obtain tetraisobutenysilane according to the scheme:



$$SiCl_4 + BrMg-CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2 \rightarrow Si(CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2)_4.$$

Isopropyl magnesium bromide enters with still greater difficulty into reaction with $SiCl_4$. Only 2 isopropyl radicals could be linked to the silicon atom by means of the organomagnesium synthesis [5, 6]. When using a more active metal (lithium), however, the isopropyl radical takes the place of 3 atoms of chlorine. A fourth isopropyl radical could not be introduced even by the action on triisopropylchlorosilane of a molecule of isopropyllithium.

Similar results were also obtained with the cyclohexyl radical. When utilizing $MgBrC_6H_{11}$ [7] only 2 cyclohexyl radicals can be linked to the silicon atom. When using cyclohexyllithium, its reaction with $SiCl_4$ can give $(C_6H_{11})_3SiCl$. It was impossible, however, to substitute the chlorine atom in $(C_6H_{11})_3SiCl$ by the organomagnesium or organolithium synthesis either with the cyclohexyl radical or with C_2H_5 [8]. The organolithium synthesis also failed to lead to tetra-α-naphthylsilane, tri-α-naphthylsilane being instead formed, according to the scheme [9]:

$$(\alpha\text{-}C_{10}H_7)_3SiOC_2H_5 + \alpha\text{-}C_{10}H_7Li \rightarrow (\alpha\text{-}C_{10}H_7)_3SiH.$$

The same silicohydrocarbon [10] was also obtained according to the scheme:

$$(\alpha\text{-}C_{10}H_7)_3SiCl + \alpha\text{-}C_{10}H_7Li \rightarrow (\alpha\text{-}C_{10}H_7)_3SiH.$$

At the same time tetra-β-naphthylsilane is obtained by analogous schemes in high yields [11].

If $SiCl_4$ is replaced by SiF_4 it is possible even by the organomagnesium synthesis to link 3 isopropyl and cyclohexyl radicals to the silicon atom [12]. By using SiF_4 it is likewise possible to obtain $(\alpha\text{-}C_{10}H_7)_3SiF$ according to the scheme [13]:

$$BrMgC_{10}H_7 + SiF_4 \rightarrow (\alpha\text{-}C_{10}H_7)_3SiF,$$

whereas with $SiCl_4$ only $(\alpha\text{-}C_{10}H_7)_2SiCl_2$ is obtained.

Taking into consideration the partial success in overcoming the difficulties by using separately either silane fluorides or organolithium compounds, we decided to make joint use of silane fluoride and organolithium compounds for synthesis of a series of tetrasubstituted silanes containing radicals which cause steric hindrance.

An attempt at the synthesis of tetra-α-napthylsilane according to the scheme:

$$(\alpha\text{-}C_{10}H_7)_2SiF_2 + 2\alpha\text{-}C_{10}H_7Li \rightarrow (\alpha\text{-}C_{10}H_7)_4Si$$

was crowned with success.

Since the synthesis was effected at high temperature, the product of synthesis was contaminated by resinous admixtures which could only be removed by chromatography.

As we know, tetracyclohexylmethane could not be obtained either by condensation of tricyclohexylchloromethane with cyclohexyl magnesium bromide or by hydrogenation of tetraphenylmethane [14]. On the other hand the synthesis of its silicon analog by the suggested scheme proceeded even after the first step, $SiF_4 + LiC_6H_{11} \rightarrow (C_6H_{11})_4Si$ (8%). Tetracyclohexylsilane was obtained in slightly better yield by a two-step synthesis according to the equation

$$(C_6H_{11})_2SiF_2 + 2LiC_6H_{11} \rightarrow (C_6H_{11})_4Si.$$

The fluorine atom in $(C_6H_{11})_3SiF$ could be substituted by the n-butyl radical in higher yield (21%).

Synthesis of tetraisobutyl- and tetraisopropylsilanes was effected according to the scheme:

$$R_3SiF + RLi \rightarrow R_4Si.$$

In the table are set forth the properties and yields of the prepared compounds.

Substance	Formula	Boiling or melting point	d_4^{20}	n_D^{20}	Yield (in %)
Tetraisopropylsilane	$C_{12}H_{28}Si$	B.p. 220-228°	0.8006	1.4472	23.8
Tetraisobutylsilane	$C_{16}H_{36}Si$	B.p. 248-250	0.7910	1.4431	63.2
Tetracyclohexylsilane	$C_{24}H_{44}Si$	M.p. 196-198	–	–	11
Tetra-α-naphthylsilane	$C_{40}H_{28}Si$	M.p. 279.6-280	–	–	24.8

The higher reactivity of fluorosilanes, in comparison with chlorosilanes, is evidently explained by the relatively high charge on fluorine and, consequently, the greater ionization of the Si – F bond in comparison with the Si – C bond [15]. The R – Li bond is also more strongly ionized than the R – MgBr bond.

EXPERIMENTAL

Synthesis of tetra-α-naphthylsilane [$(\alpha\text{-}C_{10}H_7)_4Si$]. The reaction was carried out in a three-necked, 150 ml flask, fitted with mercury-sealed stirrer, reflux condenser, dropping funnel and gas inlet tube. Naphthyllithium was prepared in the usual way from 30 g (0.14 mole) α-naphthyl bromide and 3 g (0.2 mole) lithium in 50 ml anhydrous ethyl ether. Dropwise addition was made to it of 7 g (0.02 mole) dinaphthyldifluorosilane dissolved in ether. The flask was observed to heat up. After heating the mixture for 2 hours on a water bath, 70 ml kerosene (230-250° fraction) was added, the ether was driven off and the reaction products heated on an oil bath for 25 hours. A grey precipitate came down. After the reaction mixture had been cooled to room temperature, the previously distilled-off ether was added, and decomposition was effected in the usual way.

Brown crystals separated from the ethereal layer and were filtered off. The ethereal layer was dried with calcium chloride. The naphthalene was distilled off with steam. After driving off the ether, crystals came down and were combined with the batch from the ethereal layer. Recrystallization from benzene gave 0.3 g substance with m.p. 224°; this was trinaphthylfluorosilane.

The main bulk of the crystals was insoluble in hot benzene. After 11 recrystallizations from a mixture of ligroine and chloroform, the crystals had a yellow color and melted at 100-110°. The crystals were purified by the chromatographic method. A column 30 cm high and 1.2 cm in diameter was filled with specially prepared Al_2O_3. The substance was dissolved in a mixture of ligroine (60%) and chloroform (40%), and the solution was run into the column. Elution was effected with the same mixture. 14 fractions were taken off. In fractions 5-10, after evaporating off the solvents, white crystals with m.p. 271-272° came down. After two recrystallizations from a mixture of ligroine and chloroform the crystals had m.p. 279.6-280.1°.

In all 2.9 g (24.6%) tetra-α-naphthylsilane was isolated.

6.59 mg substance: 21.66 mg CO_2; 3.19 mg H_2O; 0.72 mg SiO_2. 6.25 mg substance: 20.58 mg CO_2; 3.12 mg H_2O; 0.70 mg SiO_2. Found %: C 89.69, 89.86; H 5.41, 5.58; Si 5.12, 5.24. $C_{40}H_{28}Si$. Calculated %: C 89.51; H 5.26; Si 5.23.

Synthesis of tetraisopropylsilane $(iso\text{-}C_3H_7)_4Si$. From 8 g (1 mole) isopropyl chloride and 18 g (2.3 moles) finely flaked lithium in 150 ml anhydrous ethanol in an atmosphere of dry nitrogen was obtained isopropyllithium. To this was added dropwise 36 g (0.2 mole) triisopropylfluorosilane. The reaction mixture was then heated for 26 hours on a water bath. After cooling to room temperature and separating the unreacted lithium, the reaction products were decomposed with water. The ether layer was separated, dried and fractionally distilled to give 9.7 g (23.8%) tetraisopropylsilane with b.p. 220-228°.

Fraction with b.p. 222-224°; n_D^{20} 1.4472; d_4^{20} 0.8006; MR_D 66.83, calculated 67.32.

Found %: C 72.60, 72.22; H 13.64, 13.54; Si 13.86, 13.70. $C_{12}H_{28}Si$. Calculated %: C 72.00; H 14.00; Si 14.00.

Synthesis of tricyclohexylbutylsilane $(C_6H_{11})_3SiC_4H_9$. n-Butyllithium was prepared by the usual method from 30 g butyl bromide (0.22 mole) and 3 g (0.43 mole) finely shredded lithium. To the lithium compound was slowly added 13 g tricyclohexylfluorosilane (0.04 mole) dissolved in anhydrous ethyl ether. The reaction mixture was heated on a water bath for 16 hours; kerosene (200-220° fraction) was then added, the ether was driven off, and the residue was boiled on an oil bath for 5 hours. After cooling to room temperature, the reaction product was decomposed with water. The ether layer was driven off, dried with $CaCl_2$ and fractionated to give 3.2 g (21.9%) tricyclohexyl-n-butylsilane with b.p. 365-370°, m.p. 133-135°.

Preparation of tetracyclohexylsilane $(C_6H_{11})_4Si$. Method I. Cyclohexyllithium was prepared in a three-necked, round-bottomed liter flask from 14 g (2 moles) lithium and 100 g (0.89 mole) cyclohexyl chloride in 500 ml anhydrous ethyl ether. To the lithium compound was added dropwise, with stirring, 46 g (0.2 mole) dicyclohexylfluorosilane dissolved in 100 ml anhydrous ethyl ether. The reaction mixture was heated 10 hours on a water bath and then 11 hours on an oil bath with kerosene (190-200° fraction). The previously distilled-off ether was then added, and after working up in the usual manner the product was fractionated in vacuum to give 8.1 g (11.3%) product with m.p. 194°.

Method II. Cyclohexyllithium was prepared by the usual procedure from 100 g (0.89 mole) cyclohexyl chloride and 15 g (1 mole) lithium in a medium of ligroine. SiF_4 was passed into the solution of cyclohexyllithium in ligroine (50-75° fraction) for 4 hours The contents of the flask were heated for 6 hours on a boiling water bath. Working up in the usual way gave 7.95% yield of tetracyclohexylsilane with m.p. 196-198°.

Found %: Si 7.41, 7.87. $C_{24}H_{44}Si$. Calculated %: Si 7.77.

Synthesis of tetraisobutylsilane. Isobutyllithium was prepared from 4 g (0.29 mole) lithium and 25 g (0.27 mole) isobutyl chloride in 200 ml anhydrous ethyl ether. To it was slowly added, with stirring, 22 g (0.1 mole) triisobutylfluorosilane. Heat was released. The reaction product was heated 7 hours on a boiling water bath. Decomposition followed by the usual treatment led to separation of 16.3 g (63.2%) tetraisobutylsilane.

B.p. 248-250° (767.6 mm); d_4^{20} 0.7910; n_D^{20} 1.4431; MR_D 85.85, calculated 85.84.
Found %: C 73.7, 73.72; H 13.92; 14.02; Si 11.11, 10.85. $C_{16}H_{36}Si$. Calculated %: C 75.0; H 14.08; Si 10.92.

SUMMARY

1. It was shown that simultaneous use in the synthesis of tetrasubstituted silanes of RLi (in place of RMgBr) and SiF_4 (in place of $SiCl_4$) enables the very considerable steric hindrance to be overcome.

2. For the first time were synthesized tetraisopropylsilane, tetraisobutylsilane, tetracyclohexylsilane and tetra-α-naphthylsilane.

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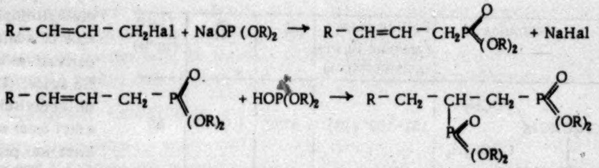
NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHONIC AND THIOPHOSPHONIC ACID

XVIII. ADDITION OF DIALKYLTHIOPHOSPHOROUS ACIDS TO IDENIC DERIVATIVES OF MALONIC AND ACETOACETIC ESTERS

A.N. Pudovik and L.I. Sidnikhina

In connection with a study of allyl rearrangements started in 1946, one of us carried out systematic investigations of reactions of salts of dialkylphosphorous acids with haloallyl derivatives. These investigations led to an interesting and unexpected result. It was found that when the reactions in question were carried out with an equimolar ratio of reactants and in presence of a small amount of a solvent, substitution of the halogen in the haloallyl compound by a phospho group also results in addition of a molecule of dialkyl phosphorous acid at the double bond of the unsaturated phosphonic ester:



$$R-CH{=}CH-CH_2Hal + NaOP(OR)_2 \rightarrow R-CH{=}CH-CH_2P(O)(OR)_2 + NaHal$$

$$R-CH{=}CH-CH_2-P(O)(OR)_2 + HOP(OR)_2 \rightarrow R-CH_2-\underset{P(O)(OR)_2}{CH}-CH_2-P(O)(OR)_2$$

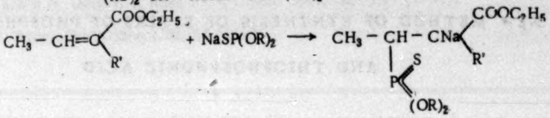
This reaction course was observed in the case of allyl bromide, the isomeric chlorobutenes, methoxychloropentenes and butoxychloropentenes [1]. This observation subsequently formed the basis of a new method of synthesis of esters of phosphonic acids. The essential feature of the method is the addition of dialkyl phosphorous and dialkylthiophosphorous acids, acid esters of alkyl and aryl phosphorous acids, phosphoacetic ester, phosphoacetone, cyanophosphomethane and their monoalkyl derivatives to unsaturated compounds of the electrophilic type. The reaction is carried out in presence of alkoxides of alkali metals. Addition takes place with great facility of the reactants mentioned to esters of unsaturated carboxylic acids – mono- and dibasic – with a double or triple bond. A large number of derivatives of esters of phospho- and thiophosphocarboxylic acids was obtained [2].

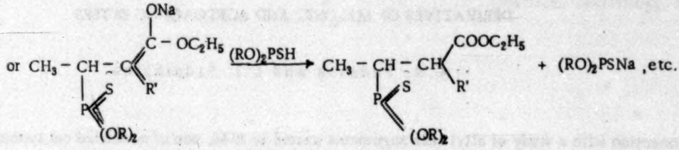
In recent years addition reactions have also been effected with unsaturated nitriles [3], ketones [4], aldehydes [5], esters of vinyl alcohols [6], esters of vinylphosphonic acid [7] and anils of various types [8]. With the help of the new method were obtained diverse esters of phospho- and diphosphocarboxylic acids, esters of phosphodicarboxylic and phosphoketocarboxylic acids, cyanophosphonic esters, esters of ketophosphonic acids, unsaturated hydroxyphosphonic esters, esters of phosphoethyl acetate, substituted aminophosphonic esters, various diphosphonoethane derivatives, and thioanalogs of all the foregoing types of compounds. The method is very simple and convenient for preparative purposes, the addition products in the majority of cases being obtained in high yields.

In a paper by one of us the addition was described of dialkylphosphorous acids to ethylidene and benzylidene malonic and ethylidene- and benzylideneacetoacetic esters [9]. It was shown that the reaction proceeds with great facility and that the addition products – esters of dialkylphosphoethyl- and dialkylphosphophenylmethylmalonic and acetoacetic acids – are obtained in yields of 65-85%. In a continuation and broadening of these investigations we decided it would be interesting to study also the addition of dialkylthiophosphorous acids to certain types of idenic derivatives of malonic and acetoacetic esters. As representatives of these acids we chose diethyl- and dibutylthiophosphorous acids. The reaction was effected in presence of sodium ethoxide and butoxide by the usual procedure as described in detail in the above-cited paper [9]. Addition of diethylthiophosphorous and dibutylthiophosphorous acids to ethylidenemalonic and ethylideneacetoacetic ester proceeded very easily and was accompanied by considerable development of heat.

The addition products – ethyl esters of α-(dialkylthiophospho)ethylmalonic and α-(dialkylthiophospho)ethylacetoacetic acids – were obtained in yields of the order of 40-50%, i.e., lower than in the case of dialkylphosphorous acids. The course of the reactions of addition of dialkylthiophosphorous acids to ethylidenemalonic and ethylideneacetoacetic esters may be represented by the following general scheme:

$$\mathrm{(RO)_2PSH + RONa \rightleftharpoons (RO)_2PSNa + ROH}$$





where $\mathrm{R = C_2H_5}$ and $\mathrm{C_4H_9}$; $\mathrm{R' = COOC_2H_5}$ and $\mathrm{COCH_3}$.

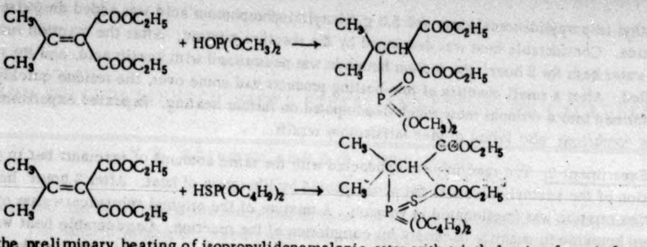
The constants of the compounds prepared are set forth in the table (first four compounds). They are viscous, colorless (in some cases faint-green) liquids with an unpleasant odor.

Preparation No.	Formulas	Boiling point (pressure in mm in parentheses)	n_D^{20}	d_4^{20}	Yield (in %)
1	$\mathrm{CH_3CHCH}\genfrac{}{}{0pt}{}{\mathrm{COCH_3}}{\mathrm{COOC_2H_5}}$ $\mathrm{S = P(OC_2H_5)_2}$	151-152° (13)	1.4720	1.0919	50
2	$\mathrm{CH_3CHCH}\genfrac{}{}{0pt}{}{\mathrm{COCH_3}}{\mathrm{COOC_2H_5}}$ $\mathrm{S = P(OC_4H_9\text{-}n)_2}$	178-180 (8)	1.4753	1.0710	45
3	$\mathrm{CH_3CHCH(COOC_2H_5)_2}$ $\mathrm{S = P(OC_2H_5)_2}$	160-161 (3)	1.4655	1.1183	52
4	$\mathrm{CH_3CHCH(COOC_2H_5)_2}$ $\mathrm{S = P(OC_4H_9\text{-}n)_2}$	190-192 (6)	1.4558	1.0616	31
5	$\mathrm{C_6H_5CHCH(COOC_2H_5)_2}$ $\mathrm{S = P(OC_2H_5)_2}$	210-212 (4)	1.4910	1.1075	51
6	$\mathrm{(CH_3)_2CCH(COOC_2H_5)_2}$ $\mathrm{S = P(OC_4H_9\text{-}n)_2}$	200-202 (4)	1.4679	1.0531	50
7	$\mathrm{(CH_3)_2CCH(COOC_2H_5)_2}$ $\mathrm{O = P(OCH_3)_2}$	170-171 (9)	1.4485	1.1870	41

In presence of sodium alkoxides, dialkylthiophosphorous acids are capable of adding on to benzylidene derivatives of malonic and acetoacetic acids. The product of addition of diethylthiophosphorous acid to the ethyl ester of benzylidenemalonic ester was prepared. It had a high b. p. (210-212° at 4 mm) and was a very viscous liquid with a faint green color and a weak, unpleasant odor.

Finally we investigated the addition of dibutylthiophosphorous acid and dimethylphosphorous acid to isopropylidenemalonic ester. In the preceeding paper [9], in which this problem was also touched upon, it was noted that dialkylphosphorous acids in presence of alkoxides of the alkali metals readily add on to isopropylidenemalonic and isopropylideneacetoacetic esters, but the addition products could not be isolated. In the course of fractionation of the reaction mixture, the viscosity gradually increased and on futher heating it changed into a very viscous, nearly solid polymeric mass.

Our experiments on the addition of dibutylthiophosphorous acid to isopropylidenemalonic ester likewise did not lead to a successful result; in course of fractionation the reaction mass invariably changed into a viscous, resinous mass which decomposed on further heating. Employment of triethylamine as the catalyst likewise did not lead to an addition product; no reaction took place, and the original components were recovered unchanged on distillation. It was observed, however, that addition of sodium butoxide to this distilled mixture of starting components caused the reaction to proceed very smoothly; fractional distillation of the reaction mixture proceeded normally and it was possible to isolate an addition product in satisfactory yield. The application of this somewhat complicated procedure to the reactions of dialkylphosphorous acids with isopropylidene derivatives of malonic and acetoacetic esters, reactions which formerly could not be realized, also had a successful outcome. The product of addition of dimethylphosphorous acid to isopropylidenemalonic ester was obtained – ethyl ester of α-methyl-α-(dimethylphospho)ethylmalonic acid – in a yield of about 50%. The reactions proceed according to the equations:



It is evident that the preliminary heating of isopropylidenemalonic ester with triethylamine frees it from certain impurities which were responsible for resinification or saponification during the subsequent distillation of the reaction products. The constants of the addition products obtained by this method are set forth in the table (last two substances).

EXPERIMENTAL

I. Addition of diethylthiophosphorous acid to ethyl ethylidenemalonate. To the reaction mixture, consisting of 6 g ethyl ethylidenemalonate and 5 g diethylthiophosphorous acid, was added dropwise a saturated solution of sodium ethoxide in anhydrous ethanol. Considerable heat was developed. The ethoxide was added at such a speed that the temperature of the reaction mixture did not rise above 80°. The solution of sodium ethoxide was introduced dropwise until its addition no longer caused heat to be developed. A short induction period was observed at the start, after which the reaction proceeded very quickly; about 15 drops ethoxide in all were required for completion of the reaction. After an hour's heating on a water bath, the reaction mixture was distilled in vacuum. Two fractionations from an Arbuzov flask gave 5.4 g ethyl ester of α-(ethylthiophospho)ethylmalonic acid with b.p. 160-161° at 3 mm.

Found %: P 8.73. $C_{13}H_{25}O_6PS$. Calculated %: P 9.11.

II. Addition of dibutylthiophosphorous acid to ethyl ethylidenemalonate. In the reaction were taken 4.7 g ethylidenemalonic ester and 5.3 g dibutylthiophosphorous acid. The reaction was conducted in presence of sodium butoxide. The reaction mixture was heated on a water bath for 3 hours and then distilled in vacuum. The fractionation gave about 5 g of a mixture of starting components and 3.1 g ethyl ester of α-(dibutylthiophospho)ethylmalonic acid with b.p. 190-192° at 6 mm.

Found %: P 7.77. $C_{17}H_{33}O_6PS$. Calculated %: P 7.83.

III. Addition of diethylthiophosphorous acid to ethyl ethylideneacetoacetate. The reaction was conducted with 5 g ethyl ethylideneacetoacetate and 5 g diethylthiophosphorous acid in presence of sodium ethoxide by the procedure described in the first experiment. Addition of the ethoxide solution to the reaction mixture was accompanied by considerable heat development. After 2 hours' heating on water bath, the reaction mixture was neutralized by addition of 1 ml of glacial acetic acid and then fractionated in vacuum. Two fractionations from a small Arbuzov flask gave 4.9 g ethyl ester of α-(diethylthiophospho)ethylacetoacetic acid with b.p. 151-152° at 13 mm.

Found %: P 10.30. $C_{12}H_{23}O_5PS$. Calculated %: P 10.00.

IV. Addition of dibutylthiophosphorous acid to ethyl ethylideneacetoacetate. To a reaction mixture consisting of 4.4 g ethyl ethylideneacetoacetate and 6 g dibutylthiophosphorous acid was slowly added dropwise a saturated solution of sodium butoxide in anhydrous butyl alcohol. Considerable heat was developed during the reaction. After 2 hours' heating on a water bath followed by neutralization of the sodium butoxide with glacial acetic acid, the reaction mixture was fractionated in vacuum to give 4.6 g ethyl α-(dibutylthiophospho)acetoacetate with b.p. 178-180° at 8 mm.

Found %: P 8.31. $C_{16}H_{31}O_5PS$. Calculated %: P 8.46.

V. Addition of diethylthiophosphorous acid to ethyl benzylidenemalonate. The reaction was performed with 6.4 g ethyl benzylidenemalonate and 4 g diethylthiophosphorous acid in presence of sodium ethoxide. After the end of the reaction and heating of the reaction mixture for an hour on a water bath, the sodium ethoxide was neutralized with acetic acid. To the mixture was added ether, the precipitate of sodium acetate was filtered off, the ether was driven off on a water bath, and the residue was distilled in vacuum to give 5.3 g ethyl phenyl-(diethylthiophospho)methylmalonate with b.p. 210-212° at 4 mm.

Found %: P 7.70. $C_{18}H_{27}O_6PS$. Calculated %: P 7.71.

VI. Addition of dibutylthiophosphorous acid to ethyl isopropylidenemalonate. Experiment 1. To a mixture of

5 g ethyl isopropylidenemalonate and 5.3 g dibutylthiophosphorous acid was added dropwise a solution of sodium butoxide. Considerable heat was developed by the reaction mixture. After the reaction mixture had been heated on a water bath for 2 hours, the sodium butoxide was neutralized with acetic acid, and the mixture was filtered and distilled. After a small quantity of low-boiling products had come over, the residue quickly thickened and was soon transformed into a resinous mass which decomposed on further heating. Repeated experiments and change of some of the conditions also failed to give satisfactory results.

Experiment 2. The reaction was conducted with the same amounts of reactants but in presence of triethylamine. Addition of the triethylamine was not accompanied by liberation of heat. After 2 hours' heating on a water bath the reaction mixture was fractionated in vacuum. A mixture of the original substances came over. To these was added sodium butoxide in quantity necessary for completion of the reaction. Considerable heat was developed in the reaction mixture during the introduction of the sodium butoxide. The mixture was then worked up as in the previous experiment. Fractionation in vacuum gave 5.1 g ethyl *a*-methyl-*a*-(dibutylthiophospho)ethylmalonate with b.p. 200-202° at 4 mm.

Found %: P 7.11. $C_{18}H_{35}O_6PS$. Calculated %: P 7.55.

VII. Addition of dimethylphosphorous acid to ethyl isopropylidenemalonate. Experiment 1. Reactants were 6.5 g ethyl isopropylidenemalonate and 3.5 g dimethylphosphorous acid. The reaction was carried out in presence of sodium methoxide and proceeded with much heat liberation. After heating on a water bath followed by neutralization of the sodium methoxide, the mixture was distilled in vacuum. A small amount of low-boiling materials came over to leave a residue which quickly changed into a thick, resinous mass. Further heating led to decomposition with evolution of a white vapor. A repeat of the experiment under the same conditions was unsuccessful.

Experiment 2. The experiment was carried out with the same amounts of reactants and catalyst, but the reaction mixture was previously heated with triethylamine. By this procedure the fractionation of the reaction mixture proceeded normally. 4.1 g ethyl *a*-methyl-*a*-(dimethylphospho)ethylmalonate was isolated with b.p. 170-171° at 9 mm.

Found %: P 9.74. $C_{12}H_{23}O_7P$ Calculated %: P 10.00.

SUMMARY

1. It was shown that dialkylthiophosphorous acids add on to ethylidenemalonic, benzylidenemalonic, isopropylidenemalonic and ethylideneacetoacetic esters.

2. The following addition products were prepared and characterized: ethyl esters of *a*-(ethylthiophospho)ethylmalonic, *a*-(dibutylthiophospho)ethylmalonic, *a*-(diethylphospho)ethylacetoacetic, *a*-(dibutylthiophospho)ethylacetoacetic, phenyl-(diethylthiophospho)methylmalonic, *a*-methyl-*a*-(dimethylphospho)ethylmalonic and *a*-methyl-*a*-(dibutylthiophospho)ethylmalonic acids.

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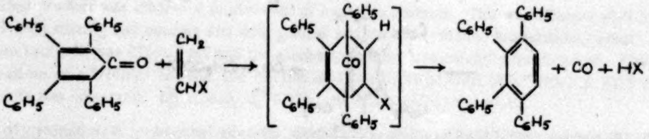
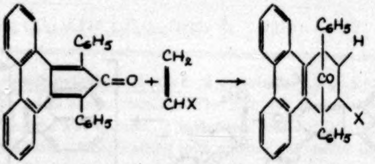
THE ACTION OF SUBSTITUTED VINYL ETHERS AND ESTERS ON CYCLONES

V.S. Abramov and A.P. Pakhomova

Abramov [1] has shown that vinyl ethers and esters can serve as the olefinic component in reactions of diene synthesis with cyclones. The diene synthesis of cyclones with vinyl compounds proceeds with cleavage of the endocarbonyl bridge and removal of alcohol in the case of vinyl ethers, or removal of an acid in the case of vinyl esters, or in general of the molecule HX, where X is any non-carbon atom.



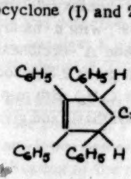
This course of the diene synthesis of vinyl compounds of the type of $CH_2{=}CHX$ is general for cyclones. The behavior of the more reactive phencyclone [2], however, differs from that of all other cyclones. Many dienophiles add on to phencyclone with greater facility than in the case of other cyclones. In reactions of diene synthesis with vinyl compounds, phencyclone gives the normal adducts with an endocarbonyl bridge.



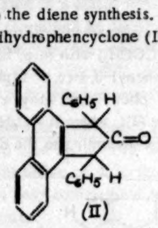
The facility with which phencyclone undergoes addition reactions and the tendency to form stable addition products with an endocarbonyl bridge, in contrast to all other cyclones, must be explained by the specificity of its structure and the specificity of the addition product formed.

Abramov and Shapshinskaya [3] studied the reaction of cyclones with aliphatic and cyclic enol-esters. It was suggested that cyclones and enol esters will react according to the diene synthesis, and since enol esters can be regarded as substituted vinyl esters, then by analogy with vinyl compounds the diene synthesis of cyclones with esters ought to proceed with cleavage of the endocarbonyl bridge and removal of the compound HX.

It was found that in the cases studied, the reactions of cyclone, acecyclone and phencyclone with enol esters do not proceed according to the diene synthesis. Cyclone and phencyclone give products of their reduction: (2,5-dihydrocyclone (I) and 2,5-dihydrophencyclone (II).



(I)



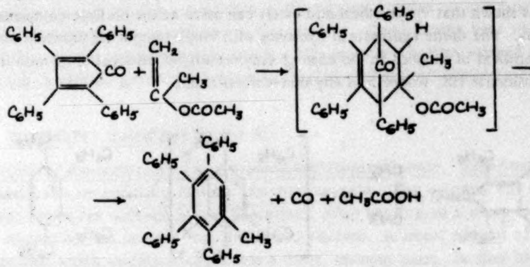
(II)

Reaction of acecyclone with enol esters is accompanied by severe resinification, and it was not possible to isolate any specific substances. The reactions were carried out in a benzene medium.

One of us [4] previously obtained dihydrocyclones by reaction of cyclones with hydrocarbons, alcohols and other organic compounds. Benzene reduces cyclones with great difficulty. In this case we must conclude that reduction takes place at the expense of enol esters. The mechanism of the reactions taking place was, however, not studied.

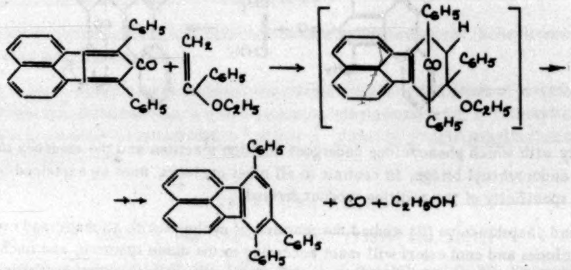
In the present research we were interested in a further study of the diene synthesis of cyclones with other substituted vinyl compounds. We regarded enol esters as β-substituted vinyl ethers which, as was shown, do not react with cyclones according to the diene synthesis. It was necessary to study the behavior in these reactions of α-substituted vinyl esters in order to be able ro reach a conclusion about the influence of the position of the substituting group on the diene synthesis of cyclones. We studied the reaction of cyclones with α-substituted vinyl ethers and esters and we established that the α-substituted vinyl ethers and esters, in contrast to the β-substituted ones, undergo the diene synthesis with cyclones.

Cyclone reacts with the α-methylvinyl ester of acetic acid according to the following scheme to give 1-methyl-2,3,4,5-tetraphenylbenzene with m.p. 185-186°:



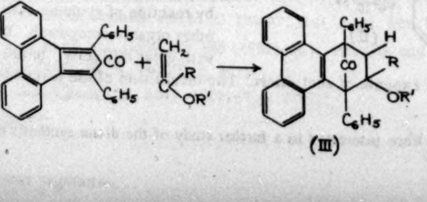
The same product is obtained by the action of α-methylvinyl ethyl ether on cyclone. Reaction of α-phenylvinyl ethyl ether with cyclone gives pentaphenylbenzene [5]. In all cases the endocarbonyl bridge and acid or alcohol are detached during the diene synthesis.

Acecyclone reacts with α-phenylvinyl ethyl ether to give 1,2,5-triphenyl-2,3-(1,8-naphthylene)-benzene with m.p. 193-194° [6]:



Acecyclone reacts with other vinyl ethers with severe resinification and specific reaction products were not isolated.

Phencyclone reacts with α-methylvinyl acetate to give 2,5-endocarbonyl-1-methyl-1-acetoxy-2,5-diphenyl-3,4-(0,0'-biphenylene)-Δ^3-cyclohexene (III, where $R = CH_3$; $R' = COCH_3$) with m.p. 238-239°; with α-methylvinyl ethyl ether it gives 2,5-endocarbonyl-1-methyl-1-ethoxy-2,5-diphenyl-3,4-(0,0'-biphenylene Δ^3-cyclohexene)-(III, where $R = C_6H_5$; $R' = C_2H_5$) with m.p. 251-252°, while with α-phenylvinyl ethyl ether it gives 2,5-endocarbonyl-1-ethoxy-1,2,5-triphenyl-3,4-(0,0'-biphenylene)-Δ^3-cyclohexene (III, where $R = C_6H_5$; $R' = C_2H_5$) with m.p. 269-270°. Phencyclone reacts with α-substituted vinyl ethers and esters according to the diene synthesis and gives normal adducts with retention of the endocarbonyl bridge:



(III)

where R is methyl or phenyl, and R′ is ethyl or acetyl.

EXPERIMENTAL

Preparation of *a*-methylvinyl ethyl ether. 15.5 g magnesium turnings was placed in a flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel; 100 ml dry ether was run in. Into the magnesium was gradually run 92 g methyl iodide. The reaction was completed by heating on a water bath. After the whole of the magnesium had reacted, the reaction mass was cooled to room temperature. With further cooling and stirring, addition was made to the methylmagnesium iodide of 150 g *a*,*β*-dibromodiethyl ether dissolved in 100 ml dry ether. During this operation heat was evolved. The course of the reaction was regulated by the speed of addition. After addition was completed, the reaction products were heated on a water bath and then treated with dilute hydrochloric acid. The ether layer was collected and dired, the ether was driven off, and the residue fractionated in vacuum. During fractionation much resinification occurred. A small amount of substance giving a positive reaction for bromine came off.

The distilled product was subjected to cleavage of hydrogen bromide. This was effected with 2% alcoholic solution of KOH with stirring and cooling and with gradual addition of *a*-methyl bromodiethyl ether. The precipitated potassium bromide was filtered off and the alcoholic solution was carefully fractionated. After three successive fractionations in a Widmer column, the fraction of *a*-methylvinyl ethyl ether with b.p. 52.5-53.5° and the following constants was collected: n_D^{20} 1.3805, d_4^{20} 0.778, MR 25.68; calculated 26.47.

Reaction of cyclone with isopropenyl acetate. Cyclone was obtained by Dilthey's method [8]. 2 g cyclone, 3 ml isopropenyl acetate and 15 ml dry ether were sealed into a tube. The tube was heated in a furnace at 130-160° for 10 hours and at 180-200° for 23 hours until the crimson color of the solution due to the cyclone had disappeared. Insignificant pressure was detected when the tube was opened. The escaping gases burned with a bluish flame. Benzene was distilled off from the reaction products, and from the residue on cooling were deposited white crystals with m.p. 182-183°, yield 1.9 g (91%). After recrystallization from glacial acetic acid they melted at 185-186°.

0.2004 g substance: 0.6878 g CO_2; 0.118 g H_2O. Found %: C 93.60; H 6.19. $C_{31}H_{24}$. Calculated %: C 93.94; H 6.06.

Reaction of cyclone with *a*-methylvinyl ethyl ether. 2 g cyclone, 1.5 ml *a*-methylvinyl ethyl ether and 15 ml benzene were sealed into a tube under carbon dioxide. The tube was heated at 180-200° for 75 hours. Insignificant pressure was detected when the tube was opened. The benzene was distilled off, and the resinous residue solidified when anhydrous ethanol was added. After washing with ethanol the residue had m.p. 180-185°, yield 1.1 g (50%). After recrystallization from glacial acetic acid the substance melted at 185-186°. A mixed test eith the product of reaction of cyclone with isopropenyl acetate melted at 185-186°.

Reaction of cyclone with *a*-phenylvinyl ethyl ether. 2 g cyclone, 3 ml *a*-phenylvinyl ethyl ether and 15 ml benzene were heated in a sealed tube at 120-150° for 5 hours and at 180-200° for 62 hours. The contents of the tube had a brown color. Slight pressure was detected on opening the tube. The benzene was distilled off from the reaction products. On cooling, the residue deposited white crystals which were filtered and washed with anhydrous enthanol; m.p. 237-240°, yield 0.7 g (29%). After recrystallization from a 1 : 1 mixture of benzene and ethanol the m.p. was 242-243°. Pentaphenylbenzene has m.p. 245-246° [8].

Reaction of acecyclone [9] with *a*-phenylvinyl ethyl ether. 2 g acecyclone, 3 ml *a*-phenylvinyl ethyl ether and 15 ml benzene were heated in a sealed tube in a furnace at 120-150° for 5 hours and at 180-200° for 24 hours. The finish of the reaction was marked by decolorization and by development of a brown color of the solution. Slight pressure was detected when the tube was opened. The benzene was dirven off and the residue deposited yellowish crystals, weight 1.8 g (78%), m.p. 182-186°. After recrystallization from benzene-ethanol they melted at 193-194°. 1,4,5-Triphenyl-2,3-(1,8,naphthylene)benzene has m.p. 195-196° [6].

Reaction of acecyclone with isopropenyl acetate. 2 g acecyclone, 3 ml isopropenyl acetate and 15 ml benzene were heated in a sealed tube at 180-200° for 30 hours. The close of the reaction was indicated by decolorization and formation of a light brown color in the solution. After opening the tube and driving off the benzene, crystallization of the residue only commenced after two weeks. Regularly fromed crystals were not obtained and the melting point was indefinite.

Reaction of phencyclone [9] with isopropenyl acetate. 2 g phencyclone, 1.5 ml isopropenyl acetate and 15 ml benzene were heated in a sealed tube on a boiling water bath for 35 hours. The termination of the reaction was marked by disappearance of the green color of the phencyclone solution. The tube was opened and the benzene was driven off. On cooling, the residue deposited white crystals weighing 2.2 g (91%) and melting at 235-238°. After recrystallization from a mixture (1:1) of alcohol and benzene, they melted at 238-239°.

0.1848 g substance: 0.5726 g CO_2; 0.0900 g H_2O. Found %: C 84.50; H 5.41. $C_{34}H_{26}O_3$. Calculated %: C 84.64; H 5.39.

Reaction of phencyclone with *a*-phenylvinyl ethyl ether. 2 g phencyclone, 3 ml *a*-phenylvinyl ethyl ether and 15 ml benzene were heated in a sealed tube in a furnace at 120-150° for 5 hours. The end of the reaction was marked by disappearance of the green color of the solution. The tube was opened and the benzene was driven off. The residue crystallized after cooling and addition of glacial acetic acid. The filtered product, after washing with ethanol, had m.p. 215-225°, yield 0.9 g (35%). After several recrystallizations from glacial acetic acid it had m.p. 269-270°.

0.1822 g substance: 0.5888 g CO_2; 0.0944 g H_2O. Found %: C 88.13; H 5.75. $C_{39}H_{30}O_2$. Calculated %: C 88.30; H 5.66.

Reaction of phencyclone with *a*-methylvinyl ethyl ether. 2 g phencyclone, 1.5 ml *a*-methylvinyl ethyl ether and 15 ml benzene were sealed into a tube under carbon dioxide. The tube was heated in a boiling water bath for 34 hours. The end of the reaction was indicated by disappearance of the green color of the solution, which changed to straw-yellow. Cooling of the tube resulted in separation of faint-yellow crystals. The tube was opened and the crystals were filtered and washed with benzene and ethanol; m.p. 200-210°; yield 0.8 g (35%); after recrystallization from a mixture of ethanol and benzene the m.p. was 251-252°.

0.1222 g substance: 0.3900 g CO_2; 0.0675 g H_2O. Found %: C 87.04; H 6.14. $C_{34}H_{28}O_2$. Calculated %: C 87.18; H 5.98.

SUMMARY

1. It was established that cyclones react with *a*-substituted vinyl ethers and esters by the diene synthesis, in contrast to β-substituted ethers or esters.

2. Cyclone and acecyclone react with *a*-substituted vinyl ethers and esters by the diene synthesis which proceeds with rupture of the endocarbonyl bridge and removal of alcohol (in the case of vinyl ethers) or of acid (in the case of vinyl esters).

3. Phencyclone reacts with vinyl ethers and esters by the diene synthesis with formation of addition products with an endocarbonyl bridge.

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ACTION OF HYDROGEN SULFIDE ON ESTERS OF ARSENOUS ACID

K. I. Kuzmin

As we know, on passing hydrogen sulfide through a solution of arsine oxides with heating, the oxygen can be replaced by sulfur to give the corresponding arsine sulfides:

$$RAsO + H_2S = RAsS + H_2O,$$

$$(R_2As)_2O + H_2S = (R_2As)_2S + H_2O.$$

Compounds so prepared were phenarsazine sulfide [1], phenylarsine sulfide [2], etc.

In this investigation we studied the action of hydrogen sulfide on esters or arsenous acid, a problem of some theoretical interest since, if the reaction

$$(RO)_3As + 3H_2S = (RS)_3As + 3H_2O$$

could be realized, this route could lead relatively simply to esters of thioarsenous acid, compounds which have hardly been investigated.

However, on passing dry hydrogen sulfide into a solution of an ester of arsenous acid in dry toluene or anhydrous diethyl ether, a yellow precipitate of arsenic sulfide came down according to the equation:

$$2(RO)_3As + 3H_2S = 6ROH + As_2S_3.$$

The reaction took place with liberation of heat. Consequently the action of hydrogen sulfide on esters of arsenous acid is completely analogous to the action of water: esters of arsenous acid are easily decomposed by hydrogen sulfide with formation of the corresponding alcohol and arsenic sulfide. Arsenic sulfide comes down quantitatively, and this suggests the possibility of utilization of this reaction for analysis of the respective organic derivatives of arsenic.

EXPERIMENTAL

The esters of arsenous acid used in our work were prepared by reaction of the corresponding alcohol with arsenic trichloride in presence of pyridine in a medium of diethyl ether. The physico-chemical constants of the prepared esters were in good agreement with the constants reported in the literature.

Action of hydrogen sulfide on tri-n-octyl arsenite. Hydrogen sulfide, previously dried by passage through three U-tubes with phosphorus pentoxide and glass wool, was passed through a solution of 6.26 g tri-n-octyl arsenite in 50 ml anhydrous diethyl ether in a round-bottomed flask fitted with a reflux condenser. Arsenic trisulfide soon came down and slight heating was observed. After passage of the hydrogen sulfide had been stopped, the precipitate of arsenic trisulfide was filtered, washed with dry ether and dried for several hours in a drying cupboard at 130°. Weight of precipitate after drying, 1.7 g (the theoretical requirement was 1.67 g).

Found %: As 60.6. As_2S_3. Calculated %: As 60.9.

The filtrate was transferred to an Arbuzov flask. The ether was driven off and the residue distilled in vacuum, when the whole residue (4.1 g) of n-octyl alcohol came over at 90° (13 mm); d_0^{20} 0.8269, n_D^{20} 1.4288.

Action of hydrogen sulfide on ethyl, isopropyl and isobutyl esters of arsenous acid. Treatment with hydrogen sulfide of solutions of triethyl arsenite, triisopropyl arsenite and triisobutyl arsenite in toluene in the above apparatus led to rapid separation of arsenic trisulfide and slight development of heat. The weight of the residue of arsenic trisulfide after drying in all cases was slightly higher than the theoretical requirement.

SUMMARY

It was established that esters of arsenous acid are decomposed with facility by hydrogen sulfide, with separation of arsenic trisulfide and the corresponding alcohol.

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SYNTHESIS OF SOME DERIVATIVES OF ALIPHATIC β-AMINO ACIDS

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The preparation of aromatic hydroxamic acids has been adequately described in the literature [1], whereas relatively little has been published about aliphatic hydroxamic acids. . Information is completely lacking about hydroxyamic acids which are derivatives of compounds with mixed functions. It was therefore a matter of interest to prepare hydroxamic acids which are derivatives of some aliphatic β-amino acids.

β-Aminodecanoic (β-aminocapric), β-aminoundecanoic and β-aminolauric acids were obtained by the method of Rodionov and Zvorykina by condensation of the corresponding aldehydes with malonic acid in presence of alcoholic ammonia [2, 3]. The ethyl esters were prepared from these acids by the usual method. Reaction of an aqueous alkaline solution of hydroxylamine with the esters of β-amino acids in presence of aqueous KOH gave the β-aminoalkylhydroxamic acids.

In the literature is reported the isolation of hydroxamic acids of the aliphatic series with the help of copper acetate followed by decomposition of the copper salt with hydrogen sulfide [4]. We isolated β-aminodecane-, β-aminoundecane- and β-aminolauric hydroxamic acids in the form of the hydrochlorides, as was described in the case of hydroxamic acids of acids of the aromatic series [5].

EXPERIMENTAL

β-Aminoundecanoic acid. A mixture of 10 g nonanal, 7.35 g malonic acid and 22 ml 5.48% alcoholic ammonia (1.21 g NH_3) was heated until carbon dioxide ceased to come off. The reaction mass was worked up with 150 ml warm water. On standing, the aqueous layer deposited white crystals which after three recrystallizations from alcohol had m.p. 196-197° with decomposition. Weight 1.0 g. The compound was soluble in hot water, alcohol, hydrochloric acid and sodium bicarbonate, insoluble in ether or acetone.

8.482 mg substance: 0.518 mg N_2 (22°, 740 mm). Found %: N 6.82. $C_{11}H_{23}O_2N$. Calculated %: N 6.96.

β-Aminolauric acid was prepared by the method described for β-aminoundecanoic acid. From 10 g capric aldehyde, 6.7 g malonic acid and 10 ml 11% alcoholic ammonia solution (1.12 g NH_3) was obtained 1.3 g β-aminolauric acid. After crystallization from alcohol it had m.p. 194-195°.

7.96 mg substance: 0.471 mg N_2 (19°, 741 mm). Found %: N 6.74. $C_{12}H_{25}O_2N$. Calculated %: N 6.51.

Ethyl β-aminodecanoate. A solution of 4 g β-aminodecanoic acid [2] in 20 ml anhydrous ethanol was saturated with hydrogen chloride until the acid had dissolved completely. The reaction mixture was heated for an hour on a water bath, after which the excess ethanol was distilled off. To the residue was added an equal volume of water (1.5-2 ml) and 10 ml ether, and the mixture shaken with intense cooling with a slight excess of 33% sodium hydroxide solution. After separation of the ethereal layer the aqueous layer was salted out with potassium carbonate and again extracted with ether. After drying the ethereal solution and removal of the solvent, the residue was thrice distilled in vacuum. The ethyl ester of β-aminodecanoic acid is an oily, viscous liquid with b.p. 151-153° at 20 mm. Weight 2.9 g.

5.152 mg substance: 12.45 mg CO_2; 5.171 mg H_2O. Found %: C 65.95; H 11.23. $C_{12}H_{25}O_2N$. Calculated %: 66.91; H 11.7.

Ethyl β-aminoundecanoate was prepared by the same method. From 6 g β-aminoundecanoic acid was obtained 4.8 g of the ethyl ester. After three distillations it had b.p. 164-167° at 20 mm.

4.289 mg substance: 10.612 mg CO_2; 4.459 mg H_2O. Found %: C 67.52; H 11.63. $C_{13}H_{27}O_2N$. Calculated %: C 68.05; H 11.87.

Ethyl β-aminolaurate was prepared by the same procedure. From 6.6 g β-aminolauric acid was obtained 4.9 g of ethyl β-aminolaurate. After three distillations it had b.p. 168-173° at 20 mm.

3.846 mg substance: 9.730 mg CO_2; 3.963 mg H_2O. Found %: C 69.04; H 11.53. $C_{14}H_{29}O_2N$. Calculated %: C 69.07; H 12.01.

β-Aminodecanehydroxamic acid hydrochloride. To a 40% aqueous solution of 0.52 g potassium hydroxide was added 0.65 g hydroxylamine hydrochloride. The precipitate of potassium chloride was separated and to the filtrate was added 1 g ethyl β-aminodecanoate and a further 0.52 g potassium hydroxide in the form of a 40% aqueous solution. The mixture was vigorously shaken until a homogeneous solution was obtained. The solution was acidified with 10% hydrochloric acid until weakly acid to congo. After addition of 30 ml anhydrous ethanol and separation of the potassium chloride, the solution was concentrated in vacuum. The residue in the form of an oily liquid was dried over phosphorus pentoxide and crystallized from dry acetone. Yield 0.5 g. β-Aminoundecanehydroxamic acid hydrochloride forms white crystals with m. p. 112°, highly soluble in alcohol, water, and hot benzene; insoluble in chloroform and ether. It gives a violet color with iron chloride.

6.325 mg substance: 0.658 N_2 (20°, 723 mm). Found %: N 11.52. $C_{10}H_{23}O_2N_2Cl$. Calculated %: N 11.70.

β-Aminoundecanehydroxamic acid hydrochloride was prepared by the same method. From 1 g ethyl β-aminoundecanoate and 0.6 g hydroxylamine hydrochloride in aqueous alkali solution (0.49 g KOH) was obtained 0.4 g β-aminoundecanehydroxamic acid hydrochloride. After crystallization from acetone it had m. p. 119-120° with decomposition.

4.146 mg substance: 0.394 ml N_2 (19°, 727 mm). Found %: N 10.69. $C_{11}H_{25}O_2N_2Cl$. Calculated %: N 11.08.

β-Aminolaurichydroxamic acid hydrochloride was prepared by the same method. From 1 g ethyl β-aminolaurate in aqueous alkali solution (0.46 g KOH) and 0.57 g hydroxylamine hydrochloride in aqueous alkali solution (0.46 g KOH) was obtained 0.5 g β-aminolaurichydroxamic acid with m. p. 118° (with decomposition) after crystallization from acetone.

6.507 mg substance: 0.618 ml N_2 (29.5°, 731 mm). Found %: N 10.31. $C_{12}H_{27}O_2N_2Cl$. Calculated %: N 10.49.

SUMMARY

1. Reaction of aldehydes with malonic acid and alcoholic ammonia by the method of Rodionov and Zvorykina gave β-aminoundecanoic and β-aminolauric acids.

2. The ethyl esters and the corresponding hydroxamic acids were prepared from the above β-amino acids and also from β-aminocapric acid.

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THE REACTION OF METHYL ACRYLATE WITH ORGANOMAGNESIUM COMPOUNDS

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In the preceding communication [1] it was shown that reaction of isopropyl magnesium bromide with methyl methacrylate gives, instead of diisopropyl isopropenyl carbinol, mainly the dimethyl ester of α,α'-dimethyl-α-isobutylglutaric acid. In the present research we investigated the possibility of formation of vinyl alcohols by the reaction of methyl acrylate with isopropyl magnesium bromide and ethyl magnesium bromide.

Reaction of isopropyl magnesium bromide with methyl acrylate gave two main products: a liquid boiling at 98-99° (2 mm) and a crystalline substance with m.p. 167.5-168°. The liquid product did not contain active hydrogen, did not react with semicarbazone acetate, and did not give a qualitative reaction for the double bond. Determination of the elementary composition, molecular weight and molecular refraction showed that the liquid product was dimethyl α-isobutylglutarate in an insufficiently pure form. It could not be purified by distillation. Hydrolysis of the ester with aqueous potassium carbonate solution gave a crystalline acid whose analytical data and melting point identified it as the α-isobutylglutaric acid prepared for the first time by Rydon [2].

The crystalline product with m.p. 167.5-168° did not react with methyl magnesium iodide or with reagents for the carbonyl group, and did not give a qualitative reaction for the double bond. The percent content of carbon and hydrogen corresponded to the general formula $C_{18}H_{30}O_3$. The neutralization equivalent was 296.6. The compound did not dissolve in benzene, glacial acetic acid, dioxane or water.

The percent content of carbon, hydrogen and silver in the silver salt corresponded to the formula $C_{18}H_{29}O_3Ag \cdot H_2O$.

Ultraviolet analysis of the alcoholic solution of the compound $C_{18}H_{30}O_3$ revealed a sharp maximum of absorption at 2940 A. From the paper of Temkin and Tikhomolova [3] we know that such a maximum is characteristic of ketones possessing substituents in the α-position to the carbonyl group, for example diisopropyl ketone. On boiling, the crystalline compound with aqueous permanganate solution, rapid decolorization took place with formation of isovaleric and oxalic acids. On the basis of the foregoing observations, we may suggest that the crystalline product is 1,3,5-triisobutylcyclohexane-2,4,6-trione. A similar type of compound has been previously prepared. Thus, Combes [4, 5] heated butyryl chloride with $AlCl_3$ and obtained a compound with the formula $C_{12}H_{18}O_3$ to which he attributed the structure of triethylcyclohexanetrione. On hydrolysis of this compound with 25% KOH solution butyrone and butyric acid were obtained. On carrying out the hydrolysis of triisobutylcyclohexanetrione under similar conditions we isolated diisoamyl ketone (isocaprone) and isocaproic acid. Consequently, the reaction of isopropyl magnesium bromide with methyl acrylate does not lead to appreciable amounts of the tertiary alcohol, diisopropylvinyl carbinol.

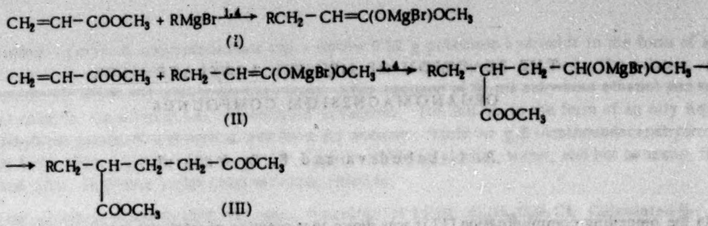
Petrov and Radzhabova [6] also point out that the action of isopropyl magnesium bromide on methyl acrylate cannot lead to a tertiary alcohol; in the subsequent experiments, therefore, we used ethyl magnesium bromide in place of isopropyl magnesium bromide. But even in this case diethylvinyl carbinol could not be isolated in the pure form.

From the mixture remaining after distilling off the ester were isolated two main products: one with b.p. 184-186° and the other with b.p. 108-109° (6 mm). The first product proved to be dibutyl ketone, and the second dimethyl α-n-propylglutarate. Hydrolysis of the ester gave α-n-propylglutaric acid. Attempts to isolate in the pure form 1,3,5-tri-n-propylcyclohexane-2,4,6-trione did not meet with success. In all cases the decomposition of the organomagnesium complex and formation of the high-boiling fractions under the most diverse conditions gave, in place of tripropyltricyclohexanetrione, products of hydrolysis of the latter – dibutyl ketone and valeric acid.

On the basis of the foregoing observations, the following general scheme for the reaction of alkyl magnesium bromides with methyl acrylate may be proposed:

A. Usual reaction of formation of tertiary alcohols.

B.

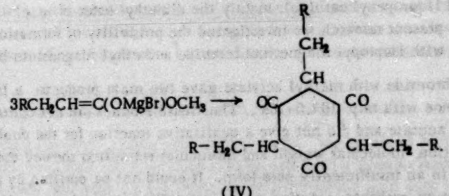


$$CH_2{=}CH{-}COOCH_3 + RMgBr \xrightarrow{1,4} RCH_2{-}CH{=}C(OMgBr)OCH_3 \quad (I)$$

$$CH_2{=}CH{-}COOCH_3 + RCH_2{-}CH{=}C(OMgBr)OCH_3 \xrightarrow{1,4} RCH_2{-}\underset{COOCH_3}{\underset{|}{CH}}{-}CH_2{-}CH(OMgBr)OCH_3 \rightarrow \quad (II)$$

$$\rightarrow RCH_2{-}\underset{COOCH_3}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}COOCH_3 \quad (III)$$

C.



(IV)

Reaction course A is not exclusively possible. During the course of the reaction in direction B, addition of the alkyl magnesium bromide to methyl acrylate takes place in the 1,4-position with formation of the magnesium bromide enolate of the ester of the monobasic acid (I), which reacts with a second molecule of methyl acrylate like a true organomagnesium compound of the type of RMgBr, with formation of the magnesium bromide enolate of the ester of the dibasic acid (II); decomposition of the latter with water gives the dimethyl ester of the substituted glutaric acid (III), hydrolysis of which leads to the substituted glutaric acid.

Evidently there is also a third reaction course C in which three molecules of (I) condense with formation of a partial ketal, a substituted cyclohexantrione thermal decomposition or hydrolysis in mild conditions of which gives the substituted cyclohexanetrione (IV). We succeeded in isolating and completely characterizing this cyclohexanetrione with R = iso-C_3H_7; with R = C_2H_5 we isolated the products of its hydrolysis – dibutyl ketone and valeric acid.

Addition of alkyl magnesium halides to unsaturated ketones and to unsaturated esters in the 1,4-position was first reported by Kohler [7]. On the other hand, it was also established that reaction of certain ketones with organomagnesium compounds does not result in addition at the carbonyl group but in enolization of the latter [8], the enolate formed behaving like a true Grignard reagent of the type of RMgX [9]. We know from the work of Kabachnik and Mastryukova [10] that magnesium enolates, incapable of changing into compounds of the RMgX type, can under many conditions, for example on methoxymethylation, also form O- and C-derivatives. According to Nesmeyanov [11] the explanation of this formation of two series of derivatives (in the absence of tautomerism) must be sought in the susceptibility of molecules containing conjugated bonds to "rearrangement of the reaction center" in the instant of reaction under the influence of the attacking reactant and under specific conditions of the reaction medium.

The successive occurrence of two reactions: 1) addition of alkyl magnesium bromide to methyl acrylate in the 1,4-position with formation of (I);and 2) reaction of (I) like a compound of the RMgX type with a second molecule of methyl acrylate, may lead in the case which we have investigated to formation of esters of substituted glutaric acids (III).

EXPERIMENTAL

Action of isopropyl magnesium bromide on methyl acrylate

To an ethereal solution of isopropyl magnesium bromide, prepared from 6 g magnesium and 31 g isopropyl bromide in 150 ml ether, was added at 0° 11 g methyl acrylate in 150 ml ether. The organomagnesium complex was decomposed with ice-water. The ether layer was decanted. The residue was treated with dilute hydrochloric acid, then with ether. The ether extract was washed with sodium carbonate and with water and added to the main ethereal solution and dried with Na_2SO_4. The liquid (17.7 g) remaining after driving off the ether boiled in the range of 25-150° (3 mm). Further temperature rise led to separation in the distillation flask of a crystalline material (2.0 g). Fractionation of the liquid in a column gave a fraction (11.0 g) with b.p. 98-99° (2 mm): n_D^{20} 1.4338, d_4^{20} 0.9759.

0.4275 g substance; 11.89 g benzene; Δt 0.880°. Found %: M 211.1. $C_{11}H_{20}O_4$. Calculated: M 216.3.

A mixture of 11 g of the substance, 200 ml water and 20 g potassium carbonate was boiled for 16 hours. To the solution, with cooling and stirring, was added 24 ml H_2SO_4 (1 : 3). The precipitated solid acid was extracted with ether to give 6.2 g crystals with m.p. 67.5–68° (from a mixture of ligroine and acetone).

0.0948 g sub.: 0.1984 g CO_2; 0.0748 g H_2O.2387 g sub.; 10.00 g acetic acid: Δt 0.250°. 0.1036 g sub.: 11.7 ml NaOH (T 0.003764). Found %: C 57.11; H 8.82; M 186.1; neut. equiv. 94.12. $C_9H_{16}O_4$. Calculated %: C 57.40; H 8.58; M 188.2; neut. equiv. 94.11.

0.1676 g sub.: 0.1612 g CO_2; 0.0557 g H_2O; 0.0866 g Ag. Found %: C 25.48; H 3.87; Ag 51.54. $C_9H_{14}O_4Ag_2 \cdot H_2O$. Calculated %: C 25.75; H 3.87; Ag 51.39.

The analytical data agreed with the formula of *a*-isobutylglutaric acid [2]. The silver salt comes down with one molecule of water of crystallization.

Examination of the crystalline residue in the distillation flask. The residue which came down in the flask with resin was separated on a porous plate in the form of white lustrous crystals with m.p. 167.5–168° (from dilute alcohol or acetone).

0.0892 g sub.: 0.2393 g CO_2; 0.0844 g H_2O. 0.2363 g sub.: 8.4 ml KOH (in alcohol, T 0.005321). Found %: C 73.21; H 10.59; neut. equiv. 296.6. $C_{18}H_{30}O_3$. Calculated %: C73.43; H 10.29; neut. equiv. 294.5. 0.1261 g sub.: 0.2358 g CO_2; 0.0017 g H_2O; 0.0329 g Ag. Found %: C 51.14; H 7.26; Ag 26.09. $C_{18}H_{29}O_3Ag \cdot H_2O$. Calculated %: C 51.57; H 7.46; Ag 25.72.

Analysis of the alcoholic solution (concentration 0.0002 M) in a SF-11 spectrophotmeter gave an absorption maximum at 2940 A (optical density of solution 1.25).

Oxidation of product with m.p. 167.5–168°. A mixture of 4 g compound and 400 ml 1% $KMnO_4$ solution was put into a three-necked flask fitted with stirrer, reflux condenser and thermometer. The solution was decolorized by boiling for 0.5 hour. The MnO_2 was filtered off, washed with hot water and extracted with ether. From the ethereal extract was obtained 1.3 g original substance with m.p. 166–167°. No neutral products were detected in the aqueous filtrate. Four fractions of volatile acids (0.8 g) were obtained and analyzed in the form of silver salts.

1st fraction, 0.1868 g sub.: 0.0964 g Ag ; Ag %: 51.62; 4th fraction, 0.496 g sub.: 0.253 g Ag; Ag % 51.00. The 2nd and 3rd fractions had intermediate contents of silver. $C_5H_9O_2Ag$. Calculated %: Ag 51.62.

From the residue of the salts was obtained an anilide with m.p. 103–105°. The data agree with the formula of isovaleric acid. After driving off the volatile acids, the solution was extracted with ether in a Soxhlet to give 0.3 g oxalic acid with m.p. 187–188°.

Hydrolysis of product with m.p. 167.5–168°. A mixture of 4 g substance, 10 g KOH and 30 ml water was boiled under reflux for 8 hours. The neutral products were distilled with steam and the distillate extracted with ether. Removal of the ether left 2 g substance distilling at 83–84° (4–5 mm):

n_D^{20} 1.4259, d_4^{20} 0.8210, MR_D 53.14. $C_{11}H_{22}O$. Calculated 53.01.

The data agreed with diisoamyl ketone (isocaprone). A semicarbazone does not come down. Analysis of the alcoholic solution (concentration 0.348 M) in the SF-11 spectrophotometer revealed an absorption maximum at 2800 A (optical density of solution 1.07), indicating the presence of a carbonyl group in the compound).

After distilling off the neutral products, the solution was acidified with the calculated amount of H_2SO_4, and the volatile acids were distilled off (0.75 g) and converted to their silver salts:

0.2431 g sub.: 0.1180 g Ag. Found %: Ag 48.54. $C_6H_{11}O_2Ag$. Calculated %: Ag 48.38.

The data agreed with those for isocaproic acid. The solution remaining after distillation of the volatile acids was extracted with ether in a Soxhlet to give 1.1 g of original substance with m. p. 163-165°.

The foregoing experiments lead to the conclusion that the compound with m.p. 167.5–168° is 1,3,5-triisobutylcyclohexane-2,4,6-trione.

Action of ethyl magnesium bromide on methyl acrylate

The organomagnesium synthesis was conducted as before using 12 g Mg, 54 g ethyl bromide and 22 g methyl acrylate in the appropriate amount of ether. Removal of the ether left 30 g product distilling at 50° (30 mm) - 120° (8 mm). In the trap was found 2 g methyl acrylate. Repeated distillation gave three fractions: 1st 130–135° 2.9 g; 2nd-184–186°, 5.0 g; 3rd 108–109° (6 mm), 6.4 g. Resin (in flask) 11 g.

Analysis of 1st fraction: 0.0720 g sub.: 9.9 ml CH_4 (15°, 761 mm). Found %: active H 0.65. $C_7H_{14}O$. Calculated %: active H 1.00.

The fraction is impure diethylvinyl carbinol.

Analysis of 2nd fraction: n_D^{20} 1.4205, d_4^{20} 0.8281, MR_D 43.52. $C_9H_{18}O$. Calculated 43.77.

The substance forms a semicarbazone with m.p. 88–89° (from dilute alcohol).

0.0709 g sub.: 12.6 ml N_2 (18°, 779.1 mm). Found %: N 21.10. $C_{10}H_{21}ON_3$ · Calculated %: N 21.02.

The data correspond to dibutyl ketone [12].

Hydrolysis of 3rd fraction. A mixture of 11 g substance, 10 g KOH and 50 ml alcohol was boiled for 6 hours. After dilution with water and evaporation of the alcohol, the product was acidified with the calculated amount of H_2SO_4. to give 5.1 g acid with m.p. 68–69° (from water).

0.1722 g sub.: 20.4 ml NaOH (T 0.003875). Found: Neut. equiv. 87.14. $C_8H_{14}O_4$· Calculated neut. equiv. 87.10. 0.2139 g sub.: 0.1186 g Ag. Found %: Ag 55.44. $C_8H_{12}O_4Ag_2$. Calculated %: Ag 55.68.

The data correspond to α-n-propylglutaric acid [13]. The residue in the flask did not crystallize.

Hydrolysis of residue. A mixture of 11 g resin, 10 g KOH and 150 ml dilute alcohol (1:1) was boiled for 6 hours. From the neutral products was isolated 1.3 g substance boiling at 184–186°. The semicarbazone had m.p. 88–89°. The data corresponded to dibutyl ketone. A silver salt was prepared from the volatile acids which distilled with steam.

0.1930 g sub.: 0.0982 g Ag. Found %: Ag 50.88. $C_5H_9O_2Ag$. Calculated %: Ag 51.62.

The anilide had m.p. 59–61°. The data corresponded to valeric acid. Decomposition of the organomagnesium complex with saturated NH_4Cl solution gave the same results.

SUMMARY

1. The reactions of methyl acrylate with ethyl magnesium bromide and isopropyl magnesium bromide were studied.

2. It was shown that the reaction proceeds simultaneously in several directions. There are formed, together with a small amount of tertiary olefinic alcohols, dimethyl esters of α-substituted glutaric acids – dimethyl α-propylglutarate and dimethyl α-isobutylglutarate, which on hydrolysis give α-propylglutaric and α-isobutylglutaric acid.

3. Formation of dimethyl esters of α-substituted glutaric acids can be attributed to the addition of alkyl magnesium bromide to methyl acrylate in the 1,4-position with formation of the enolate of the ester of a monobasic acid, and to the subsequent addition of the resultant enolate, in the form of a compound of the RMgBr type, to a second molecule of methyl acrylate, again in the 1,4-position, with formation of the enolate of the ester of a dibasic acid.

4. Condensation of three molecules of ester enolate gives partial ketals of substituted derivatives of cyclohexanetrione which, on thermal decomposition or hydrolysis, give substituted derivatives of cyclohexanetrione.

5. 1,3,5-Triisobutylcyclohexane-2,4,6-trione was isolated and characterized. Instead of 1,3,5-tri-n-propylcyclohexane-2,4,6-trione, the products of its hydrolysis – dibutyl ketone and valeric acid – were isolated.

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OXIDATION OF VINYLACETYLENIC HYDROCARBONS WITH ORGANIC HYDROPEROXIDES

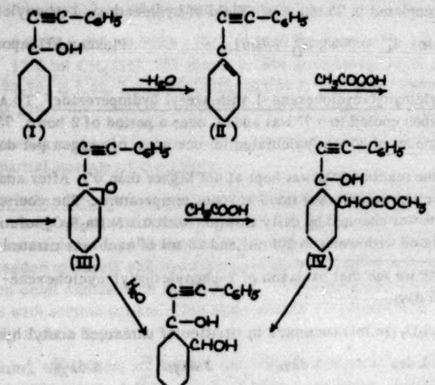
II. OXIDATION OF 1-PHENYLETHYNYLCYCLOHEXENE-1 WITH ACETYL HYDROPEROXIDE

N. M. Malenok and S. D. Kulkina

Several authors have studied the chemical transformations of oxides of cyclopentene [1], cyclohexene [2], and oxides of cyclohexenes containing various hydrocarbon radicals: methyl [3], phenyl [4], methylphenyl [5], etc.

In the present research we studied the oxide of 1-phenylethynylcyclohexene-1 (III). It was synthesized by Iotsich's method: phenylacetylene and cyclohexanone gave the alcohol, 1-phenylethynylcyclohexan-1-ol(I), which was dehydrated with potassium bisulfate to the unsaturated hydrocarbon, 1-phenylethynylcyclohexene-1 (II); this unsaturated hydrocarbon was oxidized with 75% acetyl hydroperoxide to form the oxide (III).

Treatment of the oxide with acetic acid gives the partial acetate, 1-phenylethynyl-2-acetoxy-1-cyclohexanol (IV), which, on saponification, with saturated aqueous sodium carbonate, forms the glycol, 1-phenylethynyl-cyclohexane-1,2-diol (V). The acetylenic glycol was also obtained by us by the action of water on the oxide.

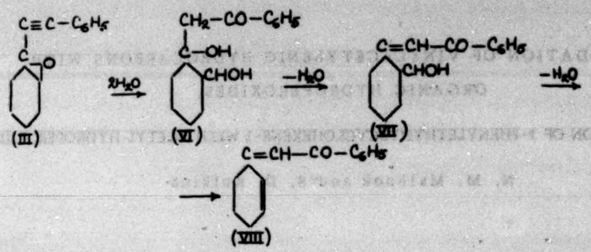


The acetylenic oxide was subjected to hydration by Kucherov's method. This reaction led to the unsaturated ketone, $\Delta^{2,3}$-cyclohexylidene-acetophenone(VIII) which decolorizes bromine in chloroform, gives a positive reaction for carbonyl group with 2,4-dinitrophenylhydrazine, and does not manifest the presence of a hydroxyl group with methyl magnesium iodide.

The formation of the unsaturated ketone apparently proceeds in the following way: treatment of the oxide with mercuric sulfate solution results in additionof two molecules of water – one at the place of rupture of the oxide ring and the other at the acetylenic bond. At first a ketoglycol, 1,2-dihydroxycylohexyl-ω-acetophenone (VI), is formed, and this then loses a molecule of water to give 2-hydroxycyclohexylidene-1-acetophenone (VII); the latter on dehydration changes into $\Delta^{2,3}$-cyclohexylideneacetophenone (VIII). (See top of next page.)

We did not isolate the two intermediate products(VI and VII).

Simultaneous hydration and dehydration by the Kucherov reaction has also been observed by other authors.



Thus, Venus-Danilova and co-workers applied this method of hydration to 1-phenylethynyl-cyclopentan-1-ol [6] and 1-phenylethynyl-cyclohexan-1-ol [7] and obtained the unsaturated ketones cyclopentylidene-acetophenone and cyclohexylidene-acetophenone.

EXPERIMENTAL

Synthesis of 1-phenylethynyl-cyclohexan-1-ol. 102 g phenylacetylene (b.p. 140-142° at 731 mm) was condensed by Iotsich's method with 98 g cyclohexanone (b.p. 154-155° at 731 mm); a solid mass was obtained from which by two distillations (b.p. 124-125° at 0.5 mm) was isolated 146 g (73%) of a crystalline substance with m.p. 61-62°, in agreement with the data of Iotsich [8] who first synthesized this alcohol.

Dehydration of 1-phenylethylnyl-cyclohexan-1-ol with potassium bisulfate. The reaction was effected by heating with fused $KHSO_4$ and simultaneous removal of the water formed in vacuum at 30° (40 mm). Dehydration of the alcohol was completed in 25 minutes. Yield of hydrocarbon, 1-phenylethynyl-cyclohexene-1, 90%.

B.p. 122-123° (0.5 mm), d_4^{20} 0.9929, n_D^{20} 1.6051. Pinkney [9] reports b.p. 117-118.5° (2 mm), d_4^{20} 0.9391, n_D^{20} 1.6033.

Oxidation of 1-phenylethynyl-cyclohexene-1 with acetyl hydroperoxide. To an ethereal solution of 51.6 g of the unsaturated hydrocarbon cooled to − 7° was added, over a period of 2 hours, 75% acetyl hydroperoxide (diluted with ether) in the amount of 30 g, as calculated for one atom of oxygen per double bond.

The temperature of the reaction mass was kept at not higher than 0°. After addition of the whole of the acetyl hydroperoxide the reaction mixture was stood at room temperature. The course of the oxidation in the main and control experiments was checked by daily titration with 0.1 N $Na_2S_2O_3$ solution. 1 ml of the main and of the control solution was diluted with water to 200 ml, and 25 ml of each was titrated.

From the data set forth we see that oxidaton of 1-phenylethynyl-cyclohexene-1 by acetyl hydroperoxide took place over a period of 5 days.

Amount of 0.1 N $Na_2S_2O_3$ (in ml) consumed in titration of unreacted acetyl hydroperoxide:

	1 day	2 days	3 days	4 days	5 days
Experiment	5.55	1.05	0.6	0.4	0.3
Control	5.55	5.35	5.0	4.8	4.7

In the course of this period the control showed a slight change of concentration of acetyl hydroperoxide. At the end of the period the reaction mixture was neutralized with 10% NaOH until its reaction was neutral. The ether layer was separated, dried for 24 hours with potassium carbonate and then filtered. The ether was driven off and the residue fractionated in vacuum. Two distillations gave 46 g (82%) substance with b.p. 144-145.5° (1 mm):

d_4^{20} 1.0581, n_D^{20} 1.5774, MR_D 62.05; calculated 59.19.
0.1071 g substance: 0.3338 CO_2; 0.0722 g H_2O. 0.1276 g substance: 0.3979 g CO_2; 0.0830 g H_2O.
0.2790 g substance; 23.52 g benzene: Δt 0.315°. Found %: C 85.00, 85.03; H 7.54, 7.28; M 193.2.
$C_{14}H_{14}O$. Calculated %: C 84.85; H 7.13; M 198.

The prepared 1-phenylethynyl-cyclohexene-1 oxide dissolves readily in ethyl ether, ethyl alcohol and chloroform; it is insoluble in water.

Action of acetic acid on 1-phenylethynyl-cyclohexene-1 oxide. 5 g of the oxide was mixed with 11.5 g glacial acetic acid; the temperature rose to 35° during this operation. The mixture was refluxed on a water bath for 4 hours at 50-55° and then boiled for 2 hours. The unreacted acetic acid was distilled off and the residual mass was twice distilled to give a remarkably viscous, yellow liquid with b.p. 164-166° (5 mm) in amount of 3.1 g (48%).

b.p. 164-166° (0.5 mm); n_D^{20} 1.5538.
0.1045 g substance: 0.2854 g CO_2; 0.0675 g H_2O. 0.1013 g substance: 0.2776 g CO_2; 0.0673 g H_2O.
0.1178 g substance: 10.5 ml CH_4 (16°, 753 mm).
0.2564 g substance: 23.96 g benzene: Δt 0.218°. Found %: C 74.48, 74.73; H 7.22, 7.41; OH 6.38; M 251.6. $C_{16}H_{18}O_3$. Calculated %: C 74.42; H 7.03; OH 6.59; M 258.

The data indicate that the substance is the partial acetate of a glycol, 1-phenylethynyl-2-acetyloxycyclohexanol-1. It is soluble in ethyl alcohol, ethyl ether, chloroform and benzene. It does not crystallize after standing for 45 days.

Hydrolysis of 1-phenylethylnyl-cyclohexene-1 oxide. 6.7 g oxide was hydrolyzed with 40 ml water containing a trace of sulfuric acid with continuous shaking and heating on a water bath at 50° for 3 hours.

A viscous mass which adhered to the walls of the flask was formed. It was extracted with ether, washed with aqueous sodium carbonate solution and with water, and then dried for a day with sodium sulfate. The ether was driven off to leave a residue with a very high viscosity and a honey-like odor which did not distil in vacuum. The compound could not be crystallized from ethyl ether, ethyl alcohol, or benzene, nor did it crystallize after prolonged standing (40 days). Only after introduction of a crystal of the same substance, prepared by hydrolysis of the partial acetate of the glycol with saturated sodium carbonate solution, did it crystallize rapidly. The crystalline product was purified by dissolving it in ethanol and precipitating with water. After three repetitions of this operation, filamentous crystals were obtained with m.p. 82.5-83°, which did not give a depression in a mixed test with the crystals obtained by hydrolysis of the partial acetate.

0.1067 g substance: 0.3027 g CO_2; 0.0708 g H_2O. 0.1120 g substance: 0.3191 g CO_2; 0.0741 g H_2O.
0.0880 g substance: 17.5 ml CH_4 (16°, 751 mm). 0.1868 g substance; 15.78 g benzene: Δt 0.27°.
Found %: C 77.37, 77.70; H 7.42, 7.41; OH 14.18; M 224.4. $C_{14}H_{16}O_2$. Calculated %: C 77.78; H 7.42; OH 15.74; M 216.

The substance analyzed is a glycol – 1 phenylethynyl-cyclohexane-1,2-diol–readily soluble in the abovementioned solvents for the partial acetate of the glycol.

Hydration of 1-phenylethynyl-cyclohexene-1 oxide by Kucherov's method. To 10 g oxide was added, with good stirring and cooling to 0°, 30 ml of a solution of $HgSO_4$ (3.5 g $HgSO_4$, 25 ml conc. H_2SO_4, 75 ml water); heat was generated and the mixture acquired a yellow color and became viscous. After 20 minutes the cooling was stopped. The reaction proceeded violently and was accompanied by crackling and marked temperature rise. The mass acquired a brown-green color and became more mobile. It was extracted with ether, washed 3 times with water and dried for 24 hours with sodium sulfate. The ether was driven off and from the residue after two distillations was isolated 4.5 g (45%) mobile liquid:

B.p. 125-127° (0.5 mm), d_{20}^{20} 1.0890, n_D^{20} 1.6092, MR_D 62.97; calculated 60.13.
0.0988 g substance; 0.3073 g CO_2; 0.0644 g H_2O. 0.1169 g substance: 0.3629 g CO_2; 0.0743 g H_2O.
0.2837 g substance; 23.70 g benzene: Δt 0.313. Found %: C 84.78, 84.67; H 7.29, 7.11; M 196.2.
$C_{14}H_{14}O$. Calculated %: C 84.85; H 7.13; M 198.

The prepared unsaturated ketone, $\Delta^{2,3}$-cyclohexylidene-acetophenone, dissolves readily in ethyl ether and chloroform, less readily in ethyl alcohol, and is insoluble in water.

With 2,4-dinitrophenylhydrazine it forms a dark-red resinous precipitate which was recrystallized from boiling ethanol with addition of ethyl acetate. After cooling, a resinous precipitate again came down. It was treated with ethyl ether and a substance was thus obtained which melted in a sealed capillary at 119-121°.

0.1012 g substance: 12.4 ml N_2 (17.5°, 757.2 mm). 0.1320 g substance: 16.4 ml N_2 (17°, 761.5 mm).
Found %: N 14.25, 14.55. $C_{20}H_{18}O_4N_4$. Calculated %: N 14.81.

The analysis agrees with the formula for $\Delta^{2,3}$-cyclohexylidene-acetophenone 2,4-dinitrophenylhydrazone.

SUMMARY

1. Oxidation of the unsaturated hydrocarbon 1-phenylethynyl-cyclohexene-1 with acetyl hydroperoxide gave its oxide in a yield of 82 %.

2. With acetic acid the oxide forms the partial acetate, 1-phenylethynyl-2-acetyloxy-cyclohexan-1-ol, which, on hydrolysis, gives the glycol, 1-phenylethynyl-cyclohexane-1,2-diol. This glycol is also obtained by the action of water on the oxide.

3. Hydration of the oxide by Kucherov's method gave the unsaturated ketone, $\Delta^{2,3}$-cyclohexylidene-acetophenone.

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* See Consultants Bureau English translation page 1193

** See Consultants Bureau English translation page 1561.

PREPARATION OF THE CYCLIC HYDRAZIDE OF MALEIC ACID AND OF SOME OF ITS DERIVATIVES

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In recent years [1] the attention of investigators has been attracted by the singular physiological activity toward plants of the cyclic hydrazide of maleic acid, the systematic name of which is 1,2-dihydropyridazinedione-3,6. In low concentrations (0.01-0.025%) it retards the flowering of various plants or even entirely prevents it [2]; in higher concentrations (0.1-0.2%) maleic acid hydrazide causes temporary stoppage of the growth of plants [1], which property is exploited for delaying the germination of fruits and potatoes during storage over long periods [3-5]. It has been proposed to employ maleic acid hydrazide for treatment of lawns in place of mechanical cutting [6]. Depending upon the concentration of the preparation employed, the retardation of plant growth is effective over a longer or shorter period. Normally a consumption of 8-10 kg per hectare of maleic acid hydrazide can serve for combating certain weeds [7]. Great interest attaches to the application of maleic acid hydrazide for treatment of lemons with the aim of raising their frost resistance [8].

Notwithstanding the undoubted practical value of 1,2-dihydropyridazinedione-3,6 in agriculture, very little has been published about its preparation.

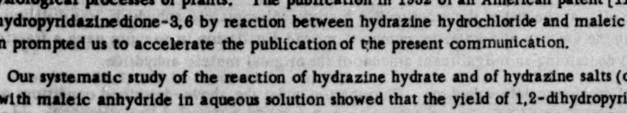
1,2-Dihydropyridazinedione-3,6 was first prepared in 1895 by Curtius [9] by reaction of hydrazine hydrate with maleic anhydride in ethanol. Under these conditions, however, the yield of 1,2-dihydropyridazinedione-3,6 did not exceed 50%. Curtius' method was later studied by Arndt, Loewe and Ergener [10] but they were unable to effect an appreciable improvement in the yield.

We commenced the study of maleic acid hydrazide as far back as 1950 in connection with its action on the physiological processes of plants. The publication in 1952 of an American patent [11] on the preparation of 1,2-dihydropyridazinedione-3,6 by reaction between hydrazine hydrochloride and maleic anhydride in aqueous solution prompted us to accelerate the publication of the present communication.

Our systematic study of the reaction of hydrazine hydrate and of hydrazine salts (of organic and inorganic acids) with maleic anhydride in aqueous solution showed that the yield of 1,2-dihydropyridazinedione-3,6 depends markedly on the final pH of the medium. The yield of 1,2-dihydropyridazinedione-3,6 rises in an acid medium and falls sharply if a strong acid is absent from the reaction medium. Good yields of 1,2-dihydropyridazinedione-3,6 (over 90%) can be obtained by starting both from salts by hydrazine with inorganic acids, and from hydrazine hydrate with addition to the reaction mixture of a small amount of a strong acid or of a salt of hydrazine with a strong acid. 1,2-Dihydropyridazinedione-3,6 can even be obtained in good yield by reaction with maleic anhydride of such poorly water-soluble salts as hydrazine sulfate.

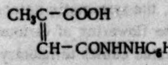
With the objective of clarifying the mechanism of formation of 1,2-dihydropyridazinedione-3,6 and of verifying the general character of the dependence which we had discovered, we studied the reaction of hydrazine and of phenylhydrazine not only with maleic anhydride but also with the anhydrides of chloro-, dichloro-, bromo- and dibromomaleic acids, and with citraconic anhydride. In all these cases, the formation of cyclic hydrazides of the respective acids most easily proceeds in an acid medium, while the anhydrides of dihalomaleic acids only give cyclic hydrazides on heating with concentrated sulfuric acid.

The data obtained indicate the possible mechanism of formation of 1,2-dihydropyridazinedione-3,6 and its derivatives. Formation of 1,2-dihydropyridazinedione-3,6 apparently proceeds in two stages: at first an acid hydrazide is formed which then cyclizes:



The first reaction proceeds in the cold with equimolecular amounts of reactants; the second proceeds with heating of the reaction mixture in presence of strong acids or of excess of maleic anhydride. Strong acids create a high hydrogen ion concentration in the reaction mixture, this being necessary for suppression of the dissociation of the maleic acid and the intermediate acid hydrazide. The high hydrogen ion concentration also catalyzes the cyclization reaction with loss of a molecule of water. In the case of dihalomaleic anhydrides, as indicated above, cyclization only occurs on heating of the intermediate acid hydrazide with concentrated sulfuric acid, since dihalomaleic acids are considerably stronger than maleic acid and a non-aqueous medium is necessary for suppression of dissociation. Two isomeric forms of the phenylhydrazide of citraconic anhydride can exist: 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6 and 1,2-dihydro-1-phenyl-4-methylpyridazinedione-3,6.

In our case it is most probable that 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6 is formed since, according to Anschütz [12], the acid phenylhydrazide of citraconic acid has the structure:



$$\begin{array}{l} CH_3C-COOH \\ \quad \| \\ CH-CONHNHC_6H_5 \end{array}$$

The chloromaleic anhydride required for synthesis of the hydrazide was prepared by direct chlorination of maleic anhydride by a slight modification of the patented method [13]. The chloromaleic anhydride obtained by the latter method was found to be contaminated with a trace of maleic anhydride, from which the chloro compound is freed with difficulty by distillation.

Direct chlorination of chloromaleic anhydride also gave dichloromaleic anhydride in good yield, while bromination of maleic anhydride and bromomaleic anhydride led to satisfactory yields of bromo- and dibromomaleic anhydrides. These compounds are extremely difficult to prepare by the methods described in the literature.

All the substituted dihydropyridazinediones were tested for inhibition of growth of shoots of wheat, radish and hemp, and were found to be practically inactive in the concentration range of 0.01-0.5%.

EXPERIMENTAL

1. Preparation of chloromaleic anhydride. A stream of chlorine was passed through a mixture of 196 g maleic anhydride and 3 g iron powder at 105°. Chlorination went on for 10 hours, after which the temperature of the mixture was raised to 190° and heating was carried out at this temperature for 5-6 hours until hydrogen chloride ceased to come off. At the end of the reaction 220 g crude chloromaleic anhydride was distilled off from the reaction flask in the vacuum of a water jet pump. A second distillation in vacuum gave a fraction boiling at 106-110° (40 mm) containing an insignificant amount of the original maleic anhydride.

2. Preparation of dichloromaleic anhydride. Chlorination under the above-described conditions of 132 g chloromaleic anhydride in presence of 1.5 g iron powder gave 140 g (84%) dichloromaleic anhydride, m.p. 118° after recrystallization from ligroine.

3. Preparation of bromomaleic anhydride. 106 g bromine was gradually added at 80° to a mixture of 98 g maleic anhydride and 1 g iron powder which was irradiated with a 300-watt lamp. After all the bromine had been added, the mixture was heated at the same temperature and irradiated for another 8 hours, after which the temperature was raised to 120-130°. At this temperature the mixture was heated for 4 hours, and then the reaction product was distilled in the vacuum of a water jet pump. A fraction boiling at 150-152° (42 mm) was collected. Yield 120 g (68%).

4. Preparation of dibromomaleic anhydride. Under the above-described conditions 35.4 g bromomaleic anhydride, 0.5 g iron powder and 34 g bromine gave 35 g dibromomaleic anhydride (68.3%) with m.p. 114°.

5. Preparation of 1,2-dihydropyridazinedione-3,6. Starting compounds for the preparation were salts of hydrazine with hydrochloric, sulfuric and oxalic acids, hydrazine hydrate and maleic anhydride. In the latter case the catalysts used were small amounts of salts of sulfuric or oxalic acids or hydrazine hydrochloride.

In all cases the yield of 1,2-dihydropyridazinedione-3,6 was 85-95%.

The reaction was carried out under the following typical conditions: To a suspension of maleic anhydride in a small amount of water was added an aqueous solution of a hydrazine salt (excluding the poorly soluble hydrazine sulfate, which was added in the form of suspension), and after stirring for 30-40 minutes the reaction mixture was boiled for 1-3 hours. On cooling, the 1,2-dihydropyridazinedione-3,6 was filtered off and purified by recrystallization from water.

6. Preparation of 1,2-dihydro-4-chloropyridazinedione-3,6. The method described for maleic hydrazide was applied to a mixture of 26.5 g chloromaleic anhydride and 26 g hydrazine sulfate in 100 ml water.

There was obtained 26.5 g (90%) 1,2-dihydro-4-chloropyridazinedione-3,6. Traces of 1,2-dihydropyridazinedione-3,6 were removed by dissolving the crude reaction product in the calculated amount of dilute aqueous alkali and adding to the solution of the sodium salts a small amount of hydrochloric acid. The precipitated 1,2-dihydropyridazinedione-3,6 (with a trace of the main product) was filtered off; the 1,2-dihydro-4-chloropyridazinedione-3,6 was then brought down from the mother liquor by acidification with hydrochloric acid. The product was finally purified by recrystallization from water. M.p. 254° (with decomposition).

Found %: Cl 24.01, 23.68; M 147.6, 147.3. Calculated %: Cl 24.21; M 146.45.

7. Preparation of 1,2-dihydro-4-bromopyridazinedione-3,6. 31 g 1,2-dihydro-4-bromopyridazinedione-3,6 was obtained by the above method from 35.4 g bromomaleic anhydride and 26 g hydrazine sulfate in 150 ml water. M.p. 251° (with decomp.) after recrystallization from water.

Found %: Br 41.32, 41.24; M 192.15, 192.6. Calculated %: Br 41.84; M 190.9

8. Preparation of 1,2-dihydro-4,5-dichloropyridazinedione-3,6. 33.4 g dichloromaleic anhydride, 26 g hydrazine sulfate and 150 ml water were stirred in a three-necked flask at room temperature for an hour, and then with heating on a boiling bath for 2 hours. After cooling, the precipitate was filtered off, dried, and heated at 150° for an hour with ten times the weight (400 g) of 80% sulfuric acid. At the conclusion of the heating, the mixture was cooled and carefully run, with cooling, into twice the volume (800-1000 ml) of water. The precipitate was filtered and washed with a little cold water. Yield 25 g (68 %) 1,2-dihydro-4,5-dichloropyridazinedione-3,6. After recrystallization from water the substance had an m.p. of 296° (with decomp.).

Found %: Cl 38.46, 38.80; M 179.0, 179.3. Calculated %: Cl 39.20, M 180.9.

9. Preparation of 1,2-dihydro-4,5-dibromopyridazinedione-3,6. Using the method described for 1,2-dihydro-4,5-dichloropyridazinedione-3,6, 25.6 g dibromomaleic acid was reacted with 13 g hydrazine sulfate in 100 ml water to give 16 g (59.2%) 1,2-dihydro-4,5-dibromopyridazinedione-3,6. Two recrystallizations from a large volume of water gave the pure compound which darkens but does not melt at 330°.

Found %: Br 59.01, 58.81; M 271.2, 271.5. Calculated %: Br 59.23; M 269.8.

10. Preparation of 1,2-dihydro-4-methylpyridazinedione-3,6. From 22.4 g citraconic anhydride and 26 g hydrazine sulfate, using the method described for 1,2-dihydropyridazinedione-3,6, was obtained 24 g 1,2-dihydro-4-methylpyridazinedione-3,6 (95%). After recrystallization from water the compound melts at 278° (with decomp.)

Found M 125.7, 125.2. Calculated: M 126.1

11. Preparation of 1,2-dihydro-2-phenylpyridazinedione-3,6. 19.6 g maleic anhydride was mixed with 28.8 g phenylhydrazine hydrochloride in 300 ml water. To the mixture was added 30 ml conc. hydrochloric acid and it was then heated to the boil. At first a transparent solution was formed, but 5-10 minutes after the start of heating an abundant precipitate began to come down. Heating was continued for 2 hours, after which the mixture was cooled and filtered. The precipitate was washed on the filter with cold water and dried. Yield 30 g (80%). After recrystallization from water followed by treatment with activated carbon the pure substance was obtained with m.p. 261°.

Found M 190.4, 190.3. Calculated: M 188.18.

12. Preparation of 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6. From 16.8 g citraconic anhydride and 21.6 g phenylhydrazine hydrochloride in 250 ml water with addition of 20 ml hydrochloric acid was obtained 25 g (82.2%) substance. After recrystallization from water, 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6 melts at 192°.

Found: M 202.0, 201.4. Calculated: M 202.2.

SUMMARY

1. A study was made of the reaction of maleic anhydride with hydrazine salts and hydrazine hydrate, using salts of hydrazine with strong acids. It was established that 1,2-dihydropyridazinedione-3,6 can be obtained in a yield of over 90% from maleic anhydride and hydrazine salts in an aqueous medium.

2. Starting from derivatives of maleic anhydride, a similar method was applied to the synthesis of a series of substituted cyclic hydrazides of maleic acid which had not previously been described in the literature.

3. A reaction mechanism is advanced for the formation of 1,2-dihydropyridazinedione-3,6 and its analogs from anhydrides and hydrazine salts.

4. All the synthesized substituted 1,2-dihydropyridazinedione-3,6 were found to be substantially inactive when tested on shoots of wheat, radish and hemp.

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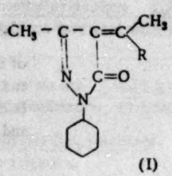
INVESTIGATIONS ON TAUTOMERIC COMPOUNDS

XVI. LABILITY OF THE HYDROGEN ATOMS IN THE PRODUCTS OF CONDENSATION OF PHENYLMETHYLPYRAZOLONE WITH KETONES

A.E. Porai-Koshits* and M.S. Dinaburg

The hydrogen atoms of the methylene group of phenylmethylpyrazolone are known to possess high lability. It appeared of interest to establish to what extent this lability is retained when the methy group is separated from the heterocycle but is in the conjugated position to the latter.

With this objective we made a study of the products of condensation of phenylmethylpyrazolone with ketones of the general formula (I) described in the previous communication [1]

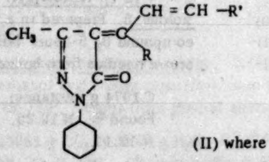


(I)

One of us had previously shown [2] that as a criterion of the lability of the hydrogen atoms of methyl groups we may employ their ability to enter into reactions with aldehydes, nitroso compounds, and diazo compounds; it was established at the time that the reaction with aldehydes is the most general one, while compounds possessing extremely high activity of the hydrogen atoms react with diazo compounds; it was natural, therefore, that we should commence the investigation of compounds of type (I) by studying their reactions with aldehydes.

Experiments show that this reaction proceeds on heating the starting substances in alcoholic solution, and in many cases in the cold; deep ruby-red or violet-red crystalline products are obtained.

The properties of the prepared compounds, their color and their analytical data indicate that formula (II) should be assigned to them.



(II) where R = C_6H_4-m-NO_2, C_6H_5, CH_3; R' = aryl.

A comparison of the course of the reaction between aldehydes and various compounds of the type of (I) reveals that the facility with which the latter enter into reaction depends, under otherwise identical conditions, on the nature of the radical R entering the compound with the ketone residue. The most active is a derivative of m-nitroacetophenone (R = C_6H_4-m-NO_2); the least active is a derivative of acetone (R = CH_3). The latter is the compound with the least pronounced acidic properties, whereas in the acetophenone derivative the acidic properties are clearly manifested. Consequently we observe here a well-marked parallelism between the ability to condense with aldehydes and the acidity of the individual compounds.

On reacting 4-[α-m-nitrophenylethylidene]- and 4-[α-phenylethylidene]-phenylmethylpyrazolone with aldehydes, the yield of reaction products and the reaction velocity increase when traces of piperidine are present. Conversely, on condensation of aldehydes with isopropylidene-phenylmethylpyrazolone the presence of piperidine leads to complete breakdown of the methyl derivative, since the latter is distinguished by instability in presence of bases.

It might have been expected that 4-isopropylidene-phenylmethylpyrazolone would be capable of reacting with aldehydes through the hydrogens of both methyl groups. It was found, however, that only one of the methyl groups is capable of reacting with aldehydes. We may note that a similar phenomenon was observed in a study of the reaction of derivatives of isoxazolone [3] and dimethylfulvene with aldehydes [4]. It is evident that due to the distribution of the influence of the hetero atoms of the ring between two methyl groups, there is a considerable lowering of the activity of the hydrogen atoms in the methyl groups, and possibly even complete inactivation of one of them.

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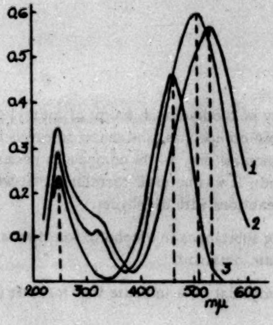
* Deceased.

One of the authors in collaboration with Khromov [5] has shown, with reference to isoxazolone derivatives, that in a number of cases the action of aldehydes is accompanied by displacement of the ketone residue by the aldehyde with formation of the corresponding arylidene derivatives of isoxazolone. We did not observe the analogous reaction of displacement of ketones from the products of their condensation with phenylmethylpyrazolone even in the case of the least stable compound — isopropylidene-phenylmethylpyrazolone.

As already mentioned, the products of condensation of aldehydes with substances of the type of (I) which we obtained are deeply colored. We thought it would be interesting to compare the depth of their color with that of arylidene derivatives of phenylmethylpyrazolone not containing the dimethyl grouping. With this objective we determined their absorption spectra, which are shown in the diagram. The curves show that introduction of the dimethyl grouping into an arylidene derivative considerably shifts the absorption maximum in the direction of longer waves (compare Curves 1 and 3 in the figure).

In addition to the absorption in the visible region of the spectrum, intense absorption is also observed in the ultraviolet with a maximum at λ = 250 mμ, which is characteristic both of phenylmethylpyrazolone itself and of many of its derivatives.



1) 4-[α-(p-Dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone; 2) 4-[α-(p-dimethylaminostyryl)-ethylidene]-phenylmethylpyrazolone; 3) 4-dimethylaminobenzylidene-phenylmethylpyrazolone.

EXPERIMENTAL

4-[α-(o-Nitrostyryl)-ethylidene]-phenylmethylpyrazolone. Prepared by 4-5 hours' boiling of 4.28 g isopropylidene-phenylmethylpyrazolone and 3.02 g o-nitrobenzaldehyde in 15 ml methanol. Yield 2.7 g (38.7%). Bright-red needles (from benzene).

0.1681 g substance: 0.4225 g CO_2; 0.0795 g H_2O; 0.1507 g substance: 16.4 ml N_2 (18°, 762 mm). Found %: C 68.97, H 5.23; N 12.10. $C_{20}H_{17}O_3N_3$. Calculated %: C 69.17; H 4.89; N 12.10.

4-[α-(p-Nitrostyryl)-ethylidene]-phenylmethylpyrazolone-5. Prepared in a similar way to the preceding compound by 5-hours' boiling. Yield 18.5%. Violet-brown needles from benzene, m.p. 171-172°.

0.1074 g substance: 11.25 ml N_2 (19°, 761 mm). Found %: N 12.25. $C_{20}H_{17}O_3N_3$. Calculated %: N 12.10.

4-[α-(p-Dimethylaminostyryl)-ethylidene]-phenylmethylpyrazolone. Prepared in the same way as before by 6-hours' boiling. Yield 26.9%, m.p. 178°. Violet-red needles (from a mixture of benzene and ligroine).

0.1431 g substance: 0.4019 g CO_2; 0.0879 g H_2O. 0.1714 g substance: 0.4797 g CO_2; 0.1034 g H_2O. 0.1259 g substance: 13.2 ml N_2 (19°, 761 mm). Found %: C 76.62, 76.30; H 6.71, 6.70; N 12.27. $C_{22}H_{23}ON_3$. Calculated %: C 76.52; H 6.66; N 12.17.

4-[α-(p-Chlorostyryl)-ethylidene]-phenylmethylpyrazolone. Prepared by boiling 2.14 g isopropylidene-phenylmethylpyrazolone, 1.4 g p-chlorobenzaldehyde and 10 ml methanol for $2^1/_2$ hours. Yield 0.65 g (19.4%). Long brown-red needles from benzene, m.p. 154-155°.

0.1429 g substance: 10.35 ml N_2 (17°, 755 mm). Found %: N 8.51. $C_{20}H_{17}ON_2Cl$. Calculated %: N 8.34.

4-[α-(p-Dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone. 5.52 g phenylethylidene-phenylmethylpyrazolone, 2.98 g p-dimethylaminobenzaldehyde, 10 ml methanol and 2 drops piperidine were boiled together. A precipitate appeared after 30 minutes Yield 6.0 g (73.7%). Lustrous, nearly black needles (from alcohol), m.p. 210-211°.

In the absence of piperidine the yield after $1^1/_2$ hours was 3.2 g (39.15%).

0.1600 g substance: 0.4688 g CO_2; 0.0903 g H_2O. 0.1565 g substance: 13.39 ml N_2 (19°, 761 mm). 0.1745 g substance: 15.50 ml N_2 (19°, 763 mm). Found %: C 79.89; H 6.26; N 10.26; 10.15. $C_{27}H_{25}ON_3$. Calculated %: C 79.C0; H 6.14; N 10.30.

4-[α-(p-Dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone. Preparation as for 4-[α-(p-dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone. Yield 63.0%. Green needles (from acetone), m.p. 167-168°.

0.1731 g substance: 0.5035 g CO_2; 0.1091 g H_2O. 0.1311 g substance: 0.3866 g CO_2: 0.0774 g H_2O. Found %: C 79.29, 80.46; H 6.79, 6.55. $C_{29}H_{29}ON_3$. Calculated %: C 80.00; H 6.68.

4-[α-(o-Nitrostyryl)-benzylidene]-phenylmethylpyrazolone. 1.38 g phenylethylidenephenylmethylpyrazolone 0.76 g o-nitrobenzaldehyde, 5 ml methanol and 1 drop piperidine were boiled 30 minutes. Yield 1.14 g (55.8%). Blue-black leaflets from glacial acetic acid or acetone, m.p. 194-195°.

0.1551 g substance: 0.4188 g CO_2; 0.0697 g H_2O. 0.1618 g substance: 0.4344 g CO_2; 0.0754 g H_2O. 0.1567 g substance: 14.0 ml N_2 (18°, 762 mm). 0.1027 g substance: 9.4 ml N_2 (19°, 763 mm). Found %: C 73.64, 73.04; H 4.88, 5.16; N 10.44, 10.58. $C_{25}H_{19}O_3N_3$. Calculated %: C 73.25; H 4.64; N 10.27.

4-[α-(p-Chlorostyryl)-benzylidene]-phenylmethylpyrazolone. 2.76 g phenylethylidene-phenylmethylpyrazolone, 1.4 g p-chlorobenzaldehyde, 1 drop piperidine and 15 ml methanol were boiled 15 minutes. Yield 1.8 g (43%). Bright-red needles from acetone, m.p. 146-147°.

0.1001 g substance: 0.0372 g AgCl. 0.1197 g substance: 0.0411 g AgCl. 0.1288 g substance: 0.0480 g AgCl. Found %: Cl 8.43, 9.20, 8.54. $C_{25}H_{19}OCl$. Calculated %: Cl 8.90.

4-[α-(o,p-Dichlorostyryl)-benzylidene]-phenylmethylpyrazolone. Prepared like the preceding compound. Yield 67%, m.p. 155-156°. Ruby-red needles from acetone.

0.1653 g substance: 0.1161 g AgCl. 0.2046 g substance: 0.1333 g AgCl. Found %: Cl 16.27, 16.25. $C_{25}H_{18}OCl_2$. Calculated %: Cl 16.39.

4-[α-(m-Methoxy-p-hydroxystyryl)-benzylidene]-phenylmethylpyrazolone. 1.38 g 4-(α-phenylethylidene)-phenylmethylpyrazolone, 0.76 g 4-hydroxy-3-methoxybenzaldehyde, 8 ml methanol and 1 drop piperidine were boiled 12 minutes. Yield 1.4 g (68.4%). Violet-red leaflets from acetic acid, m.p. 220-221°.

0.1401 g substance: 8.5 ml N_2 (19°, 762 mm). Found %: 7.11. $C_{26}H_{22}O_3N_2$. Calculated %: N 6.83.

4-[α-(m-Hydroxystyryl)-benzylidene]-phenylmethylpyrazolone. Preparation as before. Yield 78.9%. Violet-red prisms from alcohol, m.p. 215°.

0.1831 g substance: 0.5269 g CO_2; 0.0934 g H_2O. 0.1366 g substance: 8.7 ml N_2 (17°, 748 mm). 0.1820 g substance: 11.5 ml N_2 (17°, 756 mm). Found %: C 78.90; H 5.57; N 7.59, 7.40. $C_{25}H_{20}O_2N_2$. Calculated %: C 78.90; H 5.26; N 7.40.

4-[α-Styrylbenzylidene]-phenylmethylpyrazolone. 3.12 g benzaldehyde, 5.52 g phenylethylidene-phenylmethylpyrazolone, 15 ml methanol and 1 drop piperidine were brought to the boil; the mass crystallized at once. Yield 3.7 g (50.8%). M.p. 173-174°. Prisms from glacial acetic acid.

0.1313 g substance: 0.3961 g CO_2; 0.0690 g H_2O. 0.1470 g substance: 10.3 ml N_2 (17°, 753 mm). Found %: C 82.20; H 5.83; N 7.82. $C_{25}H_{20}ON_2$. Calculated %: C 82.41; H 5.49; N 7.68.

4-[α-(p-Dimethylaminostyryl)-m-nitrobenzylidene]-phenylmethylpyrazolone. 12 g p-dimethylaminobenzaldehyde, 2.6 g 4-α-(m-nitrophenylethylidene)-phenylmethylpyrazolone, 20 ml ethyl alcohol and 1-2 drops piperidine were heated to the boil, when a dense crystalline precipitate immediately came down. This was filtered and the filtrate was further heated. A fresh crop of crystals appeared and was filtered off. Total yield 2.3 g (63%). Green, bronzing needles from aqueous acetone. M.p. 150-151°.

0.1097 g substance: 0.2878 g CO_2; 0.0566 g H_2O. 0.1297 g substance: 14.0 ml N_2 (20°, 760 mm). Found %: C 71.60; H 5.80; N 12.57. $C_{27}H_{24}O_3N_4$. Calculated %: C 71.68; H 5.51; N 12.38.

Condensation of 4-(α-phenylethylidene)-phenylmethylpyrazolone with aldehydes at the ordinary temperature

1) 2.76 g methyl derivative, 1.06 g benzaldehyde, and 2 drops piperidine were mixed with 5 ml methanol and left to stand at the ordinary temperature. The solid quickly dissolved and an hour later crystals came down from the dark-red solution. These were filtered after 16 hours, washed with methanol and dried. Yield 2.9 g (79.8%). M.p. 173-174°. Violet-red prisms from acetic acid, m.p. 174°.

2) Similar results were got when the above-described reaction was carried out in the absence of a solvent.

3) 1.38 g 4-(α-phenylethylidene)-phenylmethylpyrazolone, 0.75 g p-dimethylaminobenzaldehyde, 2 drops piperidine and 10 ml methanol were stood for 3 days. The precipitated blue-black crystals were filtered off, washed with cold methanol and dried. Yield 1.89 g (93%). M.p. 209-211°.

4) In a similar manner the reactions with all the above-mentioned aldehydes can be realized.

Attempt to condense 4-isopropylidene-phenylmethylpyrazolone with 2 moles p-dimethylaminobenzaldehyde. 2.14 g (0.01 mole) 4-isopropylidene-phenylmethylpyrazolone, 2.98 g (0.02 mole) p-dimethylaminobenzaldehyde and 10 ml methanol were refluxed 6 hours. On cooling, a crystalline precipitate came down; it was filtered and washed with cold alcohol. One crystallization from 75% ethyl alcohol gave colorless leaflets, m.p. 70-72°, identified as p-dimethylaminobenzaldehyde. The dark-colored mother liquor did not crystallize after separation of the aldehyde. It was diluted with water; the oil which separated was decanted and twice extracted with boiling water. From the aqueous layer was obtained a further 0.37 g p-dimethylaminobenzaldehyde. The oil did not crystallize in the course of a long period, and only after complete drying-out of the water present did it form crystals. They were pressed to remove oil, and formed small violet needles, m.p. 174-176° (after two crystallizations from a mixture of benzene and ligroine).

SUMMARY

1. The products of condensation of phenylmethylpyrazolone with methylketones possess an extremely high lability of the hydrogen atoms in the methyl groups.

Due to the lability of the hydrogen atoms of the methyl groups, they are capable of reacting with aldehydes, forming deeply colored dimethyl derivatives.

2. Unlike the majority of compounds containing mobile hydrogen atoms, the products of condensation of phenylmethylpyrazolone with ketones can react with aldehydes even in the cold.

3. The reaction with aldehydes is catalyzed by piperidine in those cases when the original methyl derivative is stable to the action of bases.

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[3] A.E. Porai-Koshits and N.V. Khromov, J. Gen. Chem., 17, 1829 (1947).

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* T.p. = C.B. Translation pagination.

SCISSION OF CARBON-CARBON BONDS UNDER THE INFLUENCE OF DIAZO COMPOUNDS*

I. REACTION OF SOME TERTIARY AMINES OF THE TRIPHENYLMETHANE SERIES WITH DIAZO COMPOUNDS

V. V. Perekalin and L. P. Popova

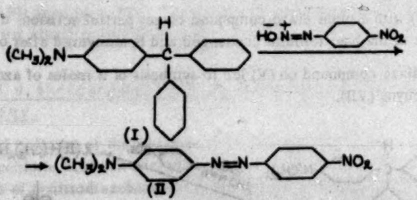
In the literature are described numerous cases of rupture of the bonds between carbon atoms, as well as between atoms of carbon and sulfur, halogens and nitrogen, occurring under the influence of diazo compounds in aromatic and more rarely in aliphatic-aromatic compounds.

In this reaction the molecule reacting with the diazo compound is cleaved, and the diazo compound residue takes the place of the part of the molecule which it displaces (for example sulfo groups [1-5], the bromine atom [6], the azo group [7], the carboxyl group [8-12], the propenyl residue [13] and the methylol group [14]). This displacement occurs when the substituent in the molecule is in the position at which the diazo group would have entered if the substituent in question had been absent, i.e. during the normal course of the azo-coupling reaction; usually this is the ortho- or para-position of the aromatic nucleus in relation to the groups promoting the reaction of azo-coupling (for example ortho or para to the dimethylamino group or the hydroxyl group).

We have investigated the character of the reaction with diazo compounds (p-nitrodiazobenzene and diazobenzene) of some tertiary amines of the triphenylmethane and diphenylmethane series.

As a rule, when carrying out these reactions aqueous solutions of the diazo compounds are added to aqueous solutions of salts of the amines (addition is made more rarely to their alcoholic solutions or aqueous suspensions); the precipitated azo dye (when the cleavage reaction takes place) was separated from the solution which was either subjected to the action of fresh portions of diazo compound or else the original amines and the products of their cleavage were isolated from it.

The simplest tertiary amine of the triphenylmethane series, 4-dimethylaminotriphenylmethane (I), was cleaved with difficulty when coupled in an aqueous alcoholic medium with p-nitrodiazobenzene and formed the azo dye 4-dimethylamino-4'-nitroazobenzene (II) from the residues of dimethylaniline and p-nitrodiazobenzene. At the same time the starting amine not entering into the reaction separated out. The second product of cleavage—diphenylcarbinol— was not isolated.



4,4'-Tetramethyldiaminotriphenylmethane (leuco base of malachite green) (III) was subjected to treatment with 1 and 2 moles of p-nitrodiazobenzene and also to stepwise reaction with the latter: after coupling with one mole of diazo compound and removal of the resultant azo dye, the solution was treated with a second mole of p-nitrodizobenzene. In each case scission of the leuco base took place without difficulty; the products of scission were formed in high yield and the azo dye (II) was isolated in high yield.

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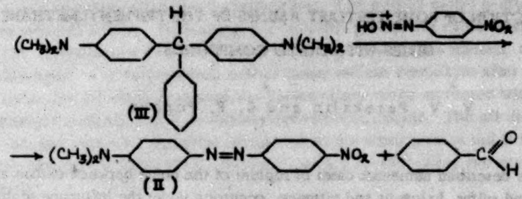
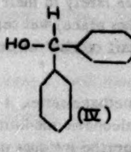
* Submitted at the sitting of the Leningrad Division of the Mendeleev All-Union Chemical Society on April 9, 1953; at the same time a communication on very similar investigation was published by E. Ziegler and G. Snatzke [15].

Treatment of base (III) with 1 mole p-nitrodiazobenzene caused partial scission with formation of 1 mole of azo dye (II) and benzaldehyde (isolated as the dimedon derivative), and there remained the non-reacted base which was oxidized to malachite green.



Reaction of (III) with 2 moles diazo compound led to its complete scission; 2 moles of the azo dye (II) and benzaldehyde were isolated.

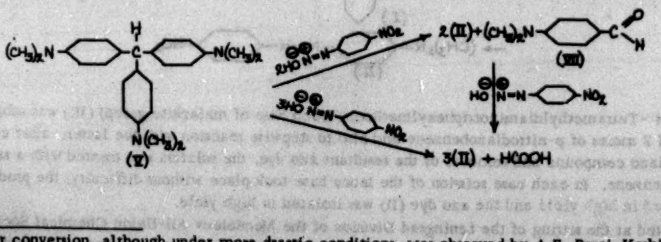
An intermediate product of the scission of (III) was possibly 4-dimethylaminodiphenylcarbinol (IV) which reacts further with the diazo compound with formation of azo dye (II) and benzaldehyde. The absence of (IV) from the products of scission of (III) may be explained in two ways: 1) carbinol (IV) in an acidic medium is converted into the original leuco base and benzaldehyde *; the rate of interaction of p-nitrodiazobenzene with carbinol (IV) is higher than the velocity of the reaction of p-nitrodiazobenzene with the leuco base (III). However, special experiments on the action on (IV) of hydrochloric acid under conditions resembling those during azo-coupling (in the cold), and also on heating, did not confirm the first hypothesis: the original carbinol was isolated quantitatively; hence the second hypothesis is apparently valid.



4,4',4"-Hexamethyltriaminotriphenylmethane (leuco base of crystal violet) (V) was treated with 1,2 and 3 moles of p-nitrodiazobenzene, and was also subjected to stepwise treatment in succession with 3 moles of the diazo compound.

Reaction of base (V) with 1 mole diazo compound causes partial scission, the products being azo dye (II) and formic acid, while part of the base remains unchanged and is recovered after oxidation to crystal violet.

Action of 2 moles diazo compound on (V) led to synthesis of 2 moles of azo dye (II) and to formation of 4-dimethylaminobenzaldehyde (VII).



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* A similar conversion, although under more drastic conditions, was observed by A.E. Porai-Koshits for carbinols of the antipyrine series [16].

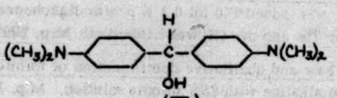
Reaction with 3 moles p-nitrodiazobenzene resulted in complete scission with formation of 3 moles azo dye (II) and formic acid.

TABLE 1

Yield of Azo Dye Formed on Scission of Amines of the Triphenylmethane Series with p-Nitrodiazobenzene

Amine	No. of moles of p-nitrodiazobenzene	Yield of azo dye (II) in % of theoretical
4-Dimethylaminotriphenylmethane (I)	1	30
4,4'-Tetramethyldiaminotriphenylmethane (III)	1	99.6
	2	92.8
4,4',4"-Hexamethyltriaminotriphenyl methane (V)	1	85.8
	2	87.0
	3	86.4

In the reaction of (V) with 1 mole diazo compound the intermediate product was 4,4'-tetramethyldiamino-diphenylcarbinol (VI); its absence from the reaction products may be explained by the higher velocity of its scission in comparison with that of the original leuco base. The hypothesis of disproportionation of carbinol (VI) to base (V) and aldehyde (VII) was not confirmed experimentally. Formation of (VII) during reaction of (V) with 2 moles diazo compound is clear evidence of the lower velocity of its scission in comparison with that of (VI).



(VI)

The dyes malachite green and crystal violet, obtained by oxidation of leuco bases (III) and (IV), did not undergo modifications under the influence of different amounts of p-nitrodiazobenzene; the positions of the long-wave maxima on the absorption curves before and after treatment with the diazo compounds were identical. The p-nitrodiazobenzene not entering into reaction was bound by 2-naphthol (Table 2). Hydrolysis of aqueous solutions of the dyes, which could have led to formation of carbinol bases, was inhibited by addition of weak hydrochloric acid solutions of the diazo compounds.

EXPERIMENTAL

1. Reaction of 4-dimethylaminotriphenylmethane (I) [17] with p-nitrodiazobenzene

a) Scission did not occur in aqueous hydrochloric acid solution, the original amine being quantitatively recovered; the diazo compound was converted into an azo dye by coupling with 2-naphthol [18].

b) In an alcoholic medium. To a solution of 0.29 g (I) in 30 ml ethyl alcohol was added 10 ml 0.1 N solution of p-nitrodiazobenzene in the course of an hour at 10-12°. After 10 hours the precipitate was filtered; it consisted of 4-dimethylamino-4'-nitroazobenzene (azo dye II). M.p. 229°; a mixed test with an authentic specimen of azo dye (II) (m.p. 230° [19]) gave m.p. 229°. Yield 0.8 g (30%). From the filtrate, after dilution with twice the amount of water and rendering alkaline with 25% ammonia solution, was isolated 0.13 g (45%) of the original amine. M.p. 130°.

2. Reaction of 4,4'-tetramethyldiazminotriphenylmethane (III) with 1 mole of p-nitrodiazobenzene.

a) Azo coupling and isolation of the azo dye. To a solution of 3.3 g leuco base in 200 ml water containing a very slight excess of hydrochloric acid (an excessive amount of hydrochloric acid slows down the reaction) was added 100 ml 0.1 N solution of p-nitrodiazobenzene in the course of an hour with stirring at 5-10°. The first few drops of diazo solution imparted a red color to the solution, and a dark-red, finely granular precipitate gradually began to come down; after 10 hours the azo dye was filtered off. M.p. 228-229°; a mixed test with a specimen of authentic azo dye (II) did not give a depression. Yield 2.69 g (99.6%).

b) Isolation of non-reacted leuco base by oxidation to malachite green. To the filtrate, acidified with 1.6 ml 37% hydrochloric acid solution and 0.8 ml 60% acetic acid, was added in small portions at 0° with stirring 1 g lead dioxide mixed with 10 ml water; the mixture was stirred 5 hours and then filtered. To the filtrate was added 0.82 zinc chloride, dissolved in a little water, and a saturated sodium chloride solution. After 24 hours the malachite green in the form of a double salt was filtered off. Yield 1.3 g (51.7%) dye. The positions of the long-wave maxima of the absorption curves of the dye obtained by oxidation of the leuco base and of malachite green were identical (λ 618 mμ).

c) Isolation of benzaldehyde. The benzaldehyde was distilled off with steam from the filtrate (after removal of the azo dye) and extracted from the distillate with ether. After removal of the ether it was dissolved in 10 ml alcohol and stirred with a solution of 1.4 g dimedon in 50 ml 50% aqueous ethyl alcohol. The solution was heated on a boiling water bath for 30 minutes and cooled. The dimedon derivative of benzaldehyde came down; m.p. 193°. A mixed test with the authentic dimedon derivative (m.p. 194° [20]) had m.p. 193°; yield 0.7g (40% calculated on the assumption that 0.5 mole leuco base had undergone scission).

3. Reaction of (III) with 2 moles p-nitrodiazobenzene

a) Azo coupling and separation of the dye. Azo coupling was carried out as described in 2a.

To a solution of leuco base was added 200 ml 0.1 n p-nitrodiazobenzene solution; azo dye (II) came down. M.p. 229°; yield 5 g (92.8%).

b) Separation of benzaldehyde. The procedure was the same as in 2c. The dimedon derivative had m.p. 193°; yield 2.65 g (75%).

4. Reaction of 4,4', 4''-hexamethyltriaminotriphenylmethane (V) with 1 mole of p-nitrodiazobenzene

a) Azo coupling and isolation of the azo dye. To a solution of 3.73 g leuco base in 10 ml 10% hydrochloric solution, diluted to 200 ml with water, was added 100 ml 0.1 N p-nitrodiazobenzene solution at 5-10° with stirring in the course of an hour. After 10 hours the azo dye (II) was filtered off. M.p. 229° Yield 2.32 g (85.8%).

b) Isolation of unreacted leuco base and qualitative determination of formic acid. The original leuco base came down when the filtrate was made alkaline with 25% amonia solution. M.p. 162.5°; a mixed sample with the authentic leuco base (m.p. 170°) melted at 165°. Yield 2.28 g (89.3%) of base (calculated on the assumption that 0.35 mole original substance had reacted). The ammoniacal solution was acidified with 10% sulfuric acid solution and distilled. Addition to the distillate of an ammoniacal solution of silver oxide and heating on a water bath caused separation of a black precipitate of metallic silver.

c) Isolation of unreacted leuco base by oxidation to crystal violet. Addition was made to the filtrate, freed from azo dye, of 5 ml 37% hydrochloric acid; after boiling 15-20 minutes, cooling and filtering, the crystal violet was salted out with sodium chloride. After 10 hours 1.66 g dye was filtered off (61% calculated on the assumption that 0.35 mole original leuco base had entered into reaction). The positions of the long-wave maxima of the absorption curves of the dye obtained by oxidation of the leuco base and of crystal violet were identical (λ 690 mμ).

5. Reaction of (V) with 2 moles p-nitrodiazobenzene

a) Azo coupling and isolation of the dye. Azo coupling was carried out as described in 2a; to a solution of leuco base was added 200 ml 1 N p-nitrodiazobenzene solution in the course of 3 hours; yield of diazo dye (II) 4.7g (87%).

b) Isolation of 4-dimethylaminobenzaldehyde (VII). 1) In the free state. Compound (VII) was isolated from the filtrate by treatment with a few milliliters of 25% ammonia solution. M.p. 72°; a mixed test with an authentic specimen of the aldehyde did not give a depression. Yield 6.9 g (61.5% on the assumption that 0.66 mole leuco base entered into reaction). 2) In the form of the dimedon derivative. The dimedon derivative of 4-dimethylaminobenzaldehyde was isolated from the filtrate (freed from azo dye). M.p. 192°; a mixed test with an authentic specimen of the dimedon derivative [20] did not give a depression. Yield 2.56 g (62% calculated for reaction of 0.66 mole leuco base).

6. Reaction of (V) with 3 moles p-nitrodiazobenzene

Azo coupling was effected as described in 4a; to a solution of the leuco base was added 300 ml 0.1 N p-nitrodiazobenzene solution in the course of 3 hours; 7.0g (86.4%) azo dye (II) was isolated. Formic acid was detected in the filtrate by the method described in 4b.

7. Reaction of malachite green (oxalic acid salt) with 1 mole p-nitrodiazobenzene

4.05 g dye was disolved at 60-70° in 300 ml water, and the solution was cooled and filtered. To the dye solution was added 100 ml acidified p-nitrodiazobenzene solution in the course of an hour with stirring at 5-10°. After 10 hours the mixture was filtered to give 3.5g (86.5%) of starting dye. The filtrate, containing unreacted p-nitrodiazobenzene, was added to a solution of 1.44 g 2-naphtol in 100 ml 1% NaOH solution; 4-nitro-1-benzeneazo-2-naphthol came down with m.p. 250° (from benzene); a mixed melting point test with the authentic azo dye did not give a depression.

Experiments in the reaction of malachite green and crystal violet with, respectively, 2 and 1, and 2 and 3 moles p-nitrodiazobenzene proceeded under analogous conditions and their results are set forth in Table 2.

TABLE 2

Reaction of malachite green and crystal violet with p-nitrodiazobenzene

Dye	Taken for reaction		Isolated			
	Dye (g)	p-Nitro-diazobenzene (moles)	original dye		4'-nitro-1-benzeneazo-2-naphthol	
			g	% of starting dye	g	% of theoretical
Malachite green	4.05	1	3.5	86.5	2.65	90.4
	4.05	2	3.0	74.1	5.5	93.8
Crystal violet	4.08	1	3.8	93.1	2.7	93.0
	4.08	2	3.2	78.4	5.2	88.7
	4.08	3	3.2	78.4	7.5	85.7

The positions of the long wave maxima of the absorption curves of malachite green and crystal violet were unchanged before and after treatment with p-nitrodiazobenzene and were respectively 618 and 500 mμ.

SUMMARY

1. It was shown that tertiary amines of the triphenylmethane series containing the dimethylamino group in the para-position to the methane bond undergo scission under the influence of active diazo compounds so that the carbon-carbon bond between the methane carbon atom and the carbon atoms of the benzene ring is broken.

2. It was established that one of the products of scission (the dimethylaniline residue) is bound by the diazo compound with formation of an azo dye, while the other separates in the free state (benzaldehyde, 4-methylaminobenzaldehyde, formic acid).

3. The ease of scission of the triphenylmethane nucleus increases with increasing number of dimethylamino groups (from one to two and three).

4. The hypothesis is advanced that certain products of scission (4-dimethylamino-diphenylcarbinol and 4,4'-tetramethyldiamino-diphenylcarbinol) were not isolated because the speed of their scission was higher than that of the original amines (leuco bases of malachite green and crystal violet).

5. It is shown that malachite green and crystal violet differ from their leuco bases in remaining unchanged under the action of diazo compounds.

6. The susceptibility to scission depends both on the structure of the amine and on the activity of the diazo compound; only active diazo compounds (p-nitrodiazobenzene) bring about cleavage.

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SCISSION OF CARBON-CARBON BONDS UNDER THE INFLUENCE OF DIAZO COMPOUNDS

II. REACTION OF SOME TERTIARY AMINES OF THE DIPHENYLETHANE SERIES AND OF DIMETHYLANILINE DERIVATIVES WITH DIAZO COMPOUNDS

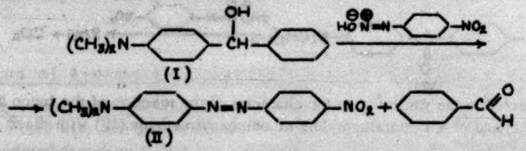
V. V. Perekalin, L. P. Popova and T. I. Abramovich

In the preceding communication [1] it was shown that reaction of leuco bases of malachite green and crystal violet with p-nitrodiazobenzene leads to derivatives of dimethylaniline, and that the intermediate products may be 4,4'-dimethylamino-diphenylmethane and 4,4'-tetramethyldiamino-triphenylmethane.

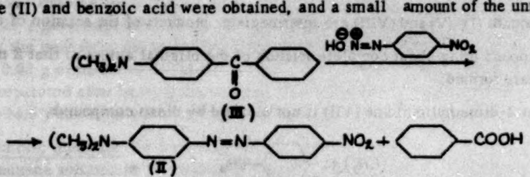
In order to obtain a more fundamental insight into the mechanism of the reation under investigation, a systematic study has been undertaken of the reaction of some tertiary amines of the diphenylmethane series and of dimethylaniline derivatives with p-nitrodiazobenzene and, in some cases, with diazobenzene.

The experimental procedure was described in the previous communication [1].

4-Dimethylamino-diphenylcarbinol (I) (suggested intermediate product of scission of the leuco base of malachite green) on coupling with 1 mole of p-nitrodiazobenzene readily undergoes scission with formation of the azo dye 4-dimethylamino-4'-nitroazobenzene (II) and benzaldehyde.



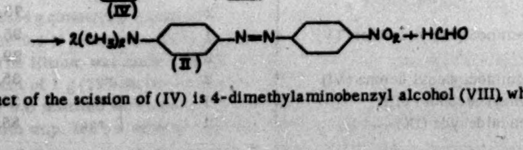
Scission of 4-dimethylamino-diphenylketone (III) proceeds with greater difficulty than that of carbinol (I). Low yields of the azo dye (II) and benzoic acid were obtained, and a small amount of the unreacted ketone was recovered.



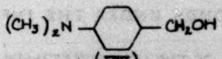
4,4-Tetramethyldiaminodiphenylmethane (IV), as shown by Sharvin and Kalyanov [2], is cleaved by two moles of p-sulfodiazobenze with formation of the azodye 4-dimethylamino-(4'-sulfo)-diazobenzene and formaldehyde.

A more detailed investigation of the scission of amine (IV) showed that scission is incomplete when using 1 mole of diazo compound (p-nitrodiazobenzene): the products are 1 mole azo dye and formaldehyde (collected in the form of the dimedon derivative), and part of the original amine remains unchanged.

Under the influence of two moles of diazo compound, amine (IV) undergoes complete scission and forms 2 moles azo dye and formaldehyde.



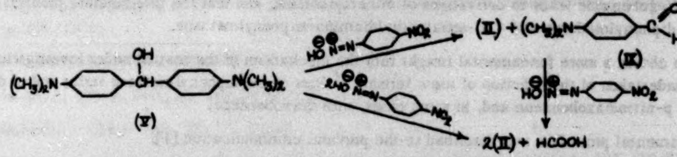
The intermediate product of the scission of (IV) is 4-dimethylaminobenzyl alcohol (VIII), which is not detected among the reaction products.



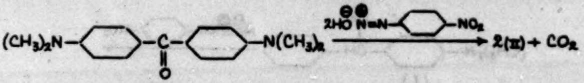
(VIII)

apparently due to the velocity of its scission being greater than that of the original amine (IV).

4,4'-Tetramethyldiamino-diphenylcarbinol (V) (hypothetical intermediate product of the scission of the leuco base of crystal violet), as reported in the literature [3], reacts with diazo compounds. With 1 mole p-nitrodiazobenzene it forms 1 mole azo dye (II) and 4-dimethylaminobenzaldehyde (IX); with 2 moles diazo compound 2 moles of azo dye (II) and formic acid are formed.



4,4'-Tetramethyldiaminodiphenyl ketone (VI) reacts with great difficulty with 2 moles of p-nitrodiazobenzene to give a low yield of azo dye (II).



(VI)

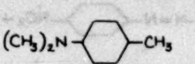
Attention should be directed to the similarity in the character of the reaction of the leuco bases of malachite green and crystal violet (see [1])and of 4,4'-tetramethyldiaminodiphenylmethane (IV) with diazo compounds:

1) 1 mole diazo compound cleaves only a part (0.5 mole) of the original amount of amine and forms 1 mole of azo dye.

2) The carbinol compounds (I), (V) and (VIII) are intermediate products of the scission of these amines.

3) 2 moles diazo compound bring about complete scission of the original amine so that 2 moles of azo dye and the corresponding aldehydes are formed.

It is a striking fact that 4-dimethyltoluidine (VII) is not cleaved by diazo compounds,



(VII)

and can not undergo with them the azo-coupling reaction in the ortho-position to the dimethylamino group. *

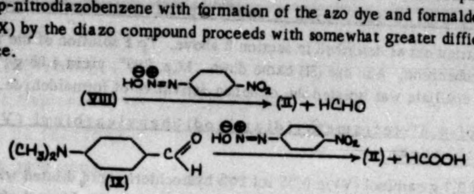
Yield of Azo Dye Formed by Scission of Amines of the Diphenylmethane Series and of Some Derivatives of Dimethylaniline by p-Nitrodiazobenzene.

Amine	number of moles of p-nitrodiazobenzene	Yield of 4-dimethylamino-4'-nitroazobenzene (II) (in % of the theoretical)
4-Dimethylaminodiphenyl carbinol (I)	1	92.6
4-Dimethylaminodiphenyl ketone (III)	1	95.0
4,4'-Tetramethyldiaminodiphenylmethane (IV)	1	92.0
	2	75.6
4,4'-Tetramethyldiaminodiphenyl carbinol (V)	1	95.7
	2	89.3
4,4'-Tetramethyldiaminodiphenyl ketone (VI)	2	35.0
4-Dimethylaminobenzyl alcohol (VIII)	1	74.0
4-Dimethylaminobenzaldehyde (IX)	1	55.0

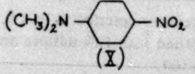
---

* This anomalous behavior of amine (VII) is apparently associated with the property of dimethylaniline and of some of its derivatives of coupling only in the para-position to the dimethylamino group, and requires special evaluation.

4-Dimethylaminobenzyl alcohol (VIII) behaves altogether differently in the azo-coupling reaction. Unlike amine (VII), it is easily cleaved by p-nitrodiazobenzene with formation of the azo dye and formaldehyde. Scission of 4-dimethylaminobenzaldehyde (IX) by the diazo compound proceeds with somewhat greater difficulty, but there is no doubt at all that scission takes place.



On the other hand, 4-dimethylamino-4'-nitrobenzene (X) does not react with p-nitrodiazobenzene in spite of variations in the reaction conditions, although easy scission of 4-dimethylaminobenzoic acid has been reported in the literature [2].



(X)

All the compounds that we investigated were subject to the action of p-nitrodiazobenzene. A less active diazo compound – diazobenzene – did not cause scission of these compounds.

The reaction medium plays an important part; excess of mineral acid leads to formation of amine salts which inhibit and sometimes stop the scission reaction.

EXPERIMENTAL

1. Reaction of 4-dimethylaminodiphenyl carbinol (I) [4] with p-nitrodiazobenzene

a) In aqueous hydrochloric acid solution. To a solution of 0.227 g carbinol in 1 ml 10% hydrochloric acid and 10 ml water, neutralized with 10% sodium acetate solution in such a manner that the reaction was weakly acidic and the whole of the carbinol remained in solution, was added 10 ml 0.1 N p-nitrodiazobenzene solution at 5-10° with stirring in the course of an hour. On adding the diazo compound the solution turned red and azo dye (II) gradually came down; this was filtered after 10 hours. M.p. 228-229°; a mixed melting point test with an authentic specimen of dye (II) (m.p. 229°) gave m.p. 229°. Yield 0.26 g (92.6%). The filtrate was distilled with steam and the distillate treated with ether; the benzaldehyde remaining after removal of the ether was dissolved in 2 ml alcohol and mixed with a solution of 0.28 g dimedon in 10 ml 50% aqueous ethyl alcohol. The dimedon derivative of benzaldehyde with m.p. 193.5° separated after heating the mixture for 30 minutes on a water bath; a mixture with the authentic derivative (m.p. 194.5°) had m.p. 194.0°. Yield 0.17 g (46.3%).

b) In an alcoholic medium. To a solution of 0.227 g carbinol (I) in 25 ml ethyl alcohol was added 100 ml 1 N p-nitrodiazobenzene solution in the course of 2 hours; after 2 hours azo dye (II) was filtered off; yield 0.26 g (99.6%). From the filtrate was isolated the dimedon derivative of benzaldehyde; yield 0.16 g (44%).

2. Reaction of 4-dimethylaminodiphenyl ketone (III) [5] with p-nitrodiazobenzene

Coupling of 1.13 g ketone (III), dissolved in 80 ml ethyl alcohol, with 25 ml of 0.2 N solution of p-nitrodiazobenzene gave the azo dye (II) which was filtered off after 10 hours. M.p. 229°; yield 0.35g (25%). 0.8 g (62%) of the original ketone was isolated from the filtrate after dilution with three times its amount of water and making alkaline with 25% ammonia solution; m.p. 89-90°; no depression in mixed melting test. The filtrate, freed from ketone, was acidified with 10% hydrochloric acid solution and treated with ether. Benzoic acid was separated from the ethereal extract. M.p. 116-117°; a mixture with authentic benzoic acid (m.p. 121°) had m.p. 118-119.

3. Reaction of 4,4'-tetramethyldiaminodiphenylmethane (IV) [6] with 1 mole of p-nitrodiazobenzene

After coupling 2.54 g amine (IV), dissolved in 7.5 ml 10% hydrochloric acid and diluted with water to a volume of 100 ml, with 100 ml 0.1 N p-nitrodiazobenzene solution, azo dye (II) was isolated (after 10 hours). M.p. 228°; yield 2.48 g (92%). The filtrate was made alkaline with 25% ammonia solution to bring down the original amine with m.p. 87° in amount of 1 g (78% on the assumption that 0.5 mole had entered into reaction). The filtrate after removal of the amine was distilled with steam. Formaldehyde was isolated from the distillate in the form of the dimedon derivative with m.p. 188°; a mixture with the authentic dimedon derivative (m.p. 189°) had m.p. 188°.

4. Reaction of amine (IV) with 2 moles p-nitrodiazobenzene

Coupling was carried out as described in section 3 above. To a solution of the amine was added 200 ml 0.1 N solution of p-nitrodiazobenzene. Azo dye (II) came down. M.p. 229°; yield 4.05 g (75%). The filtrate was steam-distilled and from the distillate was isolated the dimedon derivative of formaldehyde. M.p. 189°; yield 0.5 g (17%).

5. Reaction of 4,4'-tetramethyldiaminodiphenylcarbinol (V) [7] with 1 mole p-nitrodiazobenzene

To a solution of 2.7 g carbinol (V) in 0.75 ml 10% hydrochloric acid, diluted with water to 100 ml, was added 100 ml 0.1 N p-nitrodiazobenzene solution; after 10 hours azo dye (II) was filtered off. M.p. 228°; yield 2.59 g (95.7%). Neutralization of the filtrate with ammonia solution brought down 4-dimethylaminobenzaldehyde with m.p. 72.5°; no depression in admixture with the authentic aldehyde. Yield 0.3 g (42%).

6. Reaction of carbinol (V) with 2 moles of p-nitrodiazobenzene

Azo dye (II) was isolated by the procedure describe in Part 5. M.p. 229°; yield 4.8 g (89.3%). The filtrate was neutralized with 10% NaOH solution acidified with 10% sulfuric acid and distilled. Formic acid was detected in the distillate by the ammoniacal silver oxide test.

7. Reaction of 4,4'-tetramethyldiaminodiphenyl ketone (VI) with 1 mole of p-nitrodiazobenzene

Azo dye (II) separated after coupling 2.68 g ketone (VI), dissolved in 300 ml eyhyl alcohol, with 50 ml 0.2 N p-nitrodiazobenzene solution. M.p. 228-229° (after many recrystallizations from benzene); yield 1.62 g (30%). From the filtrate, diluted with 300 ml water and made alkaline with 25% ammonia solution, was isolated 1.2 g ketone (VI) (45% of the original amount). M.p. 171°; no depression in mixed melting test.

8. Reaction of ketone (VI) with 2 moles of p-nitrodiazobenzene

Azo dye (II) was isolated with m.p. 228-229° (yield 1.62 g; 30%) and the original ketone with m.p. 171° (1.7 g; 60% of the original amount).

9. Reaction of 4-dimethylaminobenzyl alcohol (VIII) [8] with p-nitrodiazobenzene

1.51 g alcohol (VIII) was dissolved in 5 ml 10% hydrochloric acid solution and the volume made up to 50 ml with water; addition was made of 5 ml 0.2 N p-nitrodiazobenzene solution; after 10 hours azo dye (II) was filtered off. M.p. 228°; yield 2 g (74%). From the filtrate was isolated, by the method of Part 3, the dimedon derivative of formaldehyde with m.p. 185-186°; a mixture with the authentic dimedon derivative (m.p. 188) had m.p. 187°.

10. Reaction of 4-dimethylaminobenzaldehyde (IX) with p-nitrodiazobenzene

To 1.49 g aldehyde (IX) in 3.6 ml 10% hydrochloric acid solution and 100 ml water was added 100 ml 0.1 N p-nitrodiazobenzene solution with stirring at 10-12° over a period of 2 hours; after 10 hours azo dye (II) was filtered off. M.p. 227°; yield 1.92 g (70.6%). Formic acid was detected in the filtrate by the method described in Part 6.

SUMMARY

1. It is shown that certain tertiary amines of the diphenylmethane series and some derivatives of dimethylaniline containing the dimethylamino group in the para-position to the methane bond undergo scission under the influence of active diazo compounds (p-nitrodiazobenzene); in this reaction the carbon-carbon bonds between the methane carbon atoms and the carbon atoms of the benzene rings are ruptured.

2. It was established that one of the products of scission (the dimethylaniline residue) is bound by the diazo compound with formation of an azo dye, while the other product separates in the free state (benzaldehyde, benzoic acid, formaldehyde, p-dimethylaminobenzaldehyde, formic acid).

3. The presence of only one dimethylamino group in diphenylmethane does not suffice for scission; introduction of a second dimethylamino group into the other benzene ring markedly increases the susceptibility to scission.

4. Replacement of a hydrogen atom by a hydroxyl group in the methane residue does not hinder the scission reaction; conversion of the carbinol residue into carbonyl hinders this reaction.

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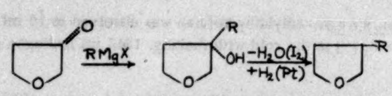
β-TETRAHYDROFURANONE AND THE SYNTHESIS OF β-ALKYL AND β-ARYLTETRAHYDROFURANS

Yu. K. Yuryev, E. M. Lukina and I. K. Korobitsyna

Up to recent times the preparation of β-alkyl- or β-aryltetrahydrofurans has been a difficult problem because the starting substances are difficultly accessible in each of the two known general methods of synthesis of these compounds. One of these methods – dehydration of the corresponding 1,4-diols – was used by Harries [1] for preparation of β-methyltetrahydrofuran and by Longinov [2] for preparation of β-propyl- and β-isohexyltetrahydrofuran. The second method – reaction of β-bromotetrahydrofuran with alkyllithiums – has been studied by one of us [3] and has been applied to the preparation of β-ethyl-, β-propyl- and β-butyl tetrahydrofurans (it was impossible to obtain β-methyltetrahydrofuran by this method).

In 1952 one of use in collaboration with Korobitsyna and Savina [4] oxidized β-hydroxytetrahydrofuran with sodium bichromate and sulfuric acid in ethereal solution and obtained the corresponding ketone β-tetrahydrofuranone, which could serve as starting substance for the organomagnesium synthesis of β-alkyl- and β-aryltetrahydrofurans. In this connection we have improved the method for its preparation. A higher yield of β-tetrahydrofuranone was obtained by oxidizing β-hydroxytetrahydrofuran with sodium bichromate and sulfuric acid in aqueous solution at 0°, and it was also shown that it enters normally into reaction with organomagnesium compounds to give the corresponding tertiary alcohols.

By reacting β-tetrahydrofuranone with n-amyl magnesium chloride and with phenyl magnesium bromide, we obtained good yields of β-hydroxy-β-n-amyltetrahydrofuran and of β-hydroxy-β-phenyltetrahydrofuran respectively.



$R = C_5H_{11}, C_6H_5$

Consequently the reaction which we have described between β-tetrahydrofuranone and organomagnesium compounds is a convenient general method of synthesis of β-alkyl- and β-aryltetrahydrofurans.

EXPERIMENTAL

1. **β-Tetrahydrofuranone.** 88 g (1 mole) β-hydroxytetrahydrofuran (b.p. 81-82° at 13 mm, n_D^{20} 1.4530, d_4^{20} 1.1036) [5] and 50 ml water were placed in a three-necked flask fitted with mechanical stirrer, dropping funnel and reflux condenser. Addition was made, with cooling with ice water and stirring, of a solution (cooled to 0°) of 100 g (0.34 mole) sodium bichromate in 250 ml water and 75 ml concentrated sulfuric acid at a rate of 2 ml per minute. After addition of the whole of the chromic mixture, cooling was stopped and stirring was continued at room temperature. Heat was liberated by the reaction mass. The mixture was stirred for another 2 hours (following fall of the temperature to room temperature), left overnight and then extracted many times with ether. The ethereal extracts were dried with potassium carbonate.

Removal of the ether followed by three fractional distillations of the residue gave 24.2 g β-tetrahydrofuranone:

B.p. 139-140° (760 mm); n_D^{20} 1.4384; d_4^{20} 1.1124; MR_D 20.21. $C_4H_6O_2$. Calculated MR_D 20.12.

Semicarbazone (from alcohol): m.p. of semicarbazone 164.5-165.5°.

Literature data: b.p. 139.4-139.8° (760 mm); n_D^{20} 1.4384; d_4^{20} 1.1124; m.p. of semicarbazone 164-165°.

21.0 g unchanged β-hydroxytetrahydrofuran was also isolated. Consequently the yield of β-tetrahydrofuranone was 28% of the theoretical calculated on the substance introduced into the reaction, and 37% calculated on the amount of reacted β-hydroxytetrahydrofuran.

No success attended attempts to prepare β-tetrahydrofuranone by catalytic dehydrogenation of β-hydroxytetrahydrofuran in presence of copper or by oxidation with atmospheric oxygen in presence of copper oxide.

2. β-Hydroxy-β-n-amyltetrahydrofuran. To an ethereal solution of n-amyl magnesium chloride, prepared from 4.9 g (0.2 mole) magnesium in 100 ml ether and 21.3 g n-amyl chloride, was added (with cooling to −10 to −12° and energetic stirring) a solution of 17.2 g (0.2 mole) β-tetrahydrofuranone in 20 ml ether.

After removal of the freezing mixture, the reaction mass was stirred for 2 1/2 hours at room temperature, heated 15 minutes on a water bath, left overnight, and decomposed with ice and ammonium chloride. After separation of the ethereal solution, the aqueous solution was repeatedly extracted with ether. The combined ethereal extracts were washed with water and dried with potassium carbonate.

The ether was driven off and the residue distilled twice to give 14.5 g (46%) β-hydroxy-β-n-amyltetrahydrofuran. The latter is a colorless liquid, with odor of mushrooms, highly soluble in ether and alcohol.

B.p. 112-112.5° (3 mm) n_D^{20} 1.4557; d_4^{20} 0.9609; MR_D 44.74. $C_9H_{18}O_2$ Calculated MR_D 44.73.

Found % : C 68.64, 68.47; H 11.50, 11.55. $C_9H_{18}O$. Calculated %: C 68.31; H 11.47.

The number of hydroxyl groups was determined by the method of Terentyev and Kupletskaya [6].

Found %: OH 10.86, 10.86. $C_9H_{17}O(OH)$. Calculated %: OH 10.76.

β-Hydroxy-β-n-amyltetrahydrofuran has not been described in the literature.

3. β-n-Amyldihydrofuran. 14 g β-hydroxy-β-n-amyltetrahydrofuran was boiled 1.5 hours with 0.02 g iodine, and the solution was then slowly distilled from a flask with a small column.

After removal of the water, the distillate was dried with anhydrous sodium sulfate and fractionated in vacuum to give 7 g β-n-amyldihydrofuran:

B.p. 62.5-65.5° (10 mm) n_D^{20} 1.4530; d_4^{20} 0.8844; MR_D 42.56. $C_9H_{16}O$. Calculated MR_D 42.74.

The product of dehydration decolorized bromine water and potassium permanganate solution.

4. β-n-Amyltetrahydrofuran. 8.5 g β-n-amyldihydrofuran was dissolved in 10 ml anhydrous ethyl alcohol and hydrogenated in presence of platinum oxide [7] in the cold with shaking. 1345 ml hydrogen (NTP) was absorbed (calculated 1518 ml).

The admixed unsaturated compound was removed by treating the product of hydrogenation with a solution of bromine in chloroform under cooling until a permanent yellow color had developed. It was then left overnight.

After driving off the chloroform, the residue was fractionated in vacuum (over sodium) to give 4.2 g (49%) β-n-amyltetrahydrofuran with the following constants:

B. p. 69-70° (12 mm) n_D^{20} 1.4378; d_4^{20} 0.8602; MR_D 43.31. $C_9H_{18}O$. Calculated MR_D 43.20.

Found %: C 75.67, 75.60; H 12.55, 12.52. $C_9H_{18}O$. Calculated %: C 75.92; H 12.74.

β-n-Amyltetrahydrofuran is not described in the literature.

5. β-Hydroxy-β-phenyltetrahydrofuran. To phenyl magnesium bromide, prepared from 39.2 g (0.25 mole) bromobenzene in 120 ml ether, was added (with cooling to −10 to −12° and with stirring) an ethereal solution of 21.5 g (0.25 mole) β-tetrahydrofuranone. The reaction mass was stirred for 3.5 hours at room temperature and then left overnight. The reaction product was isolated in the manner described above.

23.5 g (57%) β-hydroxy-β-phenyltetrahydrofuran was isolated. It is a colorless, slightly mobile liquid, soluble in ether and alcohol.

B.p. 124-124.5° (3 mm); n_D^{20} 1.5548; d_4^{20} 1.1567; MR_D 45.54. $C_{10}H_{12}O_2$. Calculated MR_D 45.74.

Found %: C 72.92, 72.93; H 7.47, 7.46. $C_{10}H_{12}O_2$. Calculated %: C 73.14; H 7.30.

β-Hydroxy-β-phenyltetrahydrofuran has not been described in the literature.

6. β-Phenyldihydrofuran. 18 g β-hydroxy-β-phenyltetrahydrofuran was dehydrated by boiling with iodine followed by distillation, when the main bulk came over at 240-242° (758 mm). Vacuum distillation gave 13.2 g (81%) β-phenyldihydrofuran with b.p. 98.5-102° (5 mm) and m.p. 39.5-40°; honey-like odor.

7. β-Phenyltetrahydrofuran. 10 g β-phenyldihydrofuran in 20 ml anhydrous alcohol was hydrogenated in presence of platinum oxide in the cold with shaking. 1410 ml (NTP) hydrogen was taken up (calculated 1540 ml).

Two fractional distillations over sodium gave 7 g (70%) β-phenyltetrahydrofuran with the following constants: B.p. 81.5-82.5° (4 mm); n_D^{20} 1.5442; d_4^{20} 1.0448; MR_D 44.78. $C_{10}H_{12}O$. Calculated MR_D 44.22.

Found %: C 81.27. 81.19; H 8.15. 8.32. $C_{10}H_{12}O$. Calculated %: C 81.08; H 8.11.

β-Phenyltetrahydrofuran is a colorless, oily liquid, soluble in alcohol, ether and acetone; it has not been reported in the literature.

SUMMARY

The preparation of β-n-amyltetrahydrofuran and of β-phenyltetrahydrofuran (neither of which are described in the literature) showed that the reaction between β-tetrahydrofuranone and organomagnesium compounds is a convenient general method of synthesis of β-alkyl- and β-aryltetrahydrofurans.

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BARBITURIC ACIDS

I. SYNTHESIS OF METHYLENE-BIS-5-ALKYLBARBITURIC ACIDS

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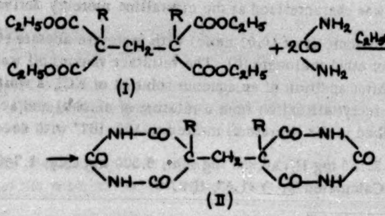
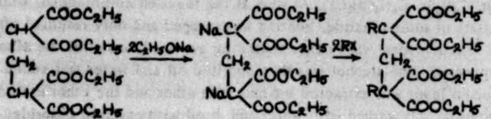
Methylene-bis-barbituric acid and its homologs had not been described in the literature until recently; it was only in 1949 that Gisling and Schwarzenbach [1] prepared methylene-bis-barbituric acid by reduction of methyl-bis-barbituric acid as well as by the usual method – the action of urea on methylene-bis-malonic ester in presence of sodium ethoxide.

In the present research, a series of previously undescribed methylene-bis-5-alkyl-barbituric acids (II) was synthesized by the action of urea on methylene-bis-alkylmalonic esters (I).



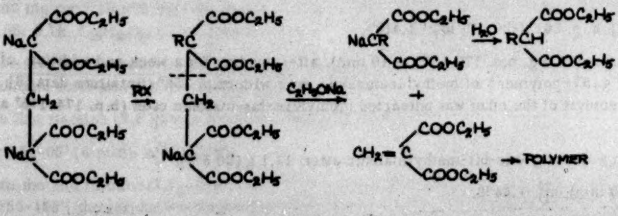
(where R = CH_3, C_2H_5, C_3H_7, C_4H_9 or $C_6H_5CH_2$)

The starting methylene-bis-alkylmalonic esters were prepared by reaction of primary halides with methylene-bis-sodium malonic esters:



The yield of dialkyl esters was 20-40% of the theoretical. Secondary products of the reaction, isolated in all cases, were the corresponding monoalkylmalonic esters (in yields of 11 to 40% of the theoretical calculated on the methylene-bis-malonic ester) and the crystalline polymer of methylenemalonic ester, first described by N. D. Zelinksy [2].

Formation of these substances may be the result of scission of the intermediately formed sodium derivative of the monoalkylated methylene-bis-malonic ester under the action of sodium ethoxide, with formation of sodium alkylmalonic ester and methylenemalonic ester which is later transformed into the crystalline polymer*:



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* A paper by Welch [3] draws attention to the possibility of such a scission. The author considered that on distillation in presence of caustic alkali, methylene-bis-malonic ester itself is cleaved with formation of malonic ester and methylenemalonic ester.

It should be noted that when using secondary bromides (iso-C_3H_7Br) or primary bromides with a branched structure (iso-C_4H_9Br; iso-$C_5H_{11}Br$) the reaction proceeded only according to the second scheme and the main reaction products were monoalkylmalonic esters (yields up to 53% of the theoretical); dialkylated methylene-bis-malonic esters were not formed.

Alkylation of methylene-bis-malonic ester has been described by Dressel [4] but without information about the yields of the alkylation products and their constants; his paper makes no mention of the formation of secondary products of reaction – monoalkylmalonic esters and the polymer of methylenemalonic ester.

EXPERIMENTAL

Methylene-bis-malonic ester was prepared in a yield of 60-70% of the theoretical by reaction of malonic ester with paraform in presence of 10% alcoholic KOH solution [3].

B.p. 174-175° (5 mm); n_D^{20} 1.4425; d_4^{20} 1.119 MR_D 78.57. Calculated MR_D 78.08.

Literature data [5]: b.p. 192° (12 mm); d_4^{20} 1.116.

Methylene-bis-malonic easter was characterized as the crystalline mercury derivative.

Mercuration of methylene-bis-malonic ester (0.01 mole) with mercuric acetate (0.02 mole) was effected by the method described for mercuration of ethyl malonate [6]. The resultant viscous oil was separated from the aqueous layer and dissolved in dilute alcohol. After addition of an aqueous solution of KCl, a white precipitate of the dichloromercuri-derivative came down. After recrystallization from a mixture of alcohol and acetone the methylene-bis-chloromercurimalonic ester (not described in the literature) melted at 165-167° with decomposition.

8.450 mg sub.: 6.760 mg CO_2; 2.150 mg H_2O; 6.950 mg sub.; 5.520 mg CO_2; 1.740 mg H_2O. Found %: C 21.83, 21.68; H. 2.84, 2.80. $C_{15}H_{22}O_8Hg_2Cl_2$. Calculated %: C 21.43; H 2.76.

Alkylation of methylene-bis-malonic ester

To sodium ethoxide (4.6 g Na in 150 ml anhydrous ethyl alcohol) was added methylene-bis-malonic ester (34 g, 0.1 mole) in small portions, followed dropwise (with stirring and heating on a water bath) by 0.3 mole alkyl halide (RX = CH_3I, C_2H_5Br, C_3H_7Br, C_4H_9Br, $C_6H_5CH_2Cl$). As soon as the reaction commenced, which was visible from the formation of a white precipitate of sodium halide, heating was stopped and only resumed after the whole of the alkyl halide had been added. The reaction mass was further heated for several hours until the alkaline reaction (to litmus) had almost completely disappeared. The alcohol was then distilled off and water was added to the residue; the oily layer was separated; the aqueous layer was extracted 3 times with ether, and the ether extracts added to the oil layer. The whole of the ethereal solution was washed with water and dried with calcium chloride; after driving off the ether the residual oil was distilled in vacuum.

Below are set forth the results obtained in each alkylation experiment.

1. Methylene-bis-methylmalonic ester. Three main fractions were obtained from the product of reaction between methylene-bis-sodium malonic ester and methyl bromide after fractional distillation in vacuum:

The 1st fraction (2.0 g, b.p. 78-79° at 10 mm; n_D^{20} 4132), judging by its constants was a secondary product of the reaction – monomethylmalonic ester (yield 11.5% of the theoretical calculated on the methylene-bis-malonic ester).

Literature data [7]: b. p. 201.2-201.4°; $n_D^{18.7}$ 1.4137.

From the 2nd fraction (14.0 g, b.p. 170-175° at 10 mm), after standing for a week and addition of a few drops of ether, was isolated 1.0 g (5%) polymer[*] of methylenemalonic ester with m.p. 156° (literature data [8]: m.p. 154-156). The oil remaining after removal of the ether was unreacted methylene-bis-malonic ester (b.p. 174-175° at 5 mm; n_D^{20} 1.4430).

The third fraction was methylene-bis-methylmalonic ester, 11.1 g (30.8%).

B. p. 190-191° (10 mm); n_D^{20} 1.4470.

Literature data [4]: b.p. 191-192° (12 mm).

Since the close-boiling original methylene-bis-malonic ester might have been present as impurity in the prepared methylene-bis-methylmalonic ester, we purified the latter by the mercuration reaction.

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[*] Methylmalonic ester readily polymerizes to a crystalline substance with m.p. 156°, to which is attributed the structure of a polymer containing 10-11 structural units [9].

To the methylene-bis-methylmalonic ester (fraction boiling at 190-191° at 10 mm) was added a solution of mercuric acetate in distilled water. The mixture was boiled 6 hours, and after cooling aqueous KCl solution was run in; a small amount of white precipitate came down (methylene-bis-chloromercurimalonic ester). The purified methylene-bis-methylmalonic ester was extracted with ether, the ether was driven off, and the dried residue was vacuum-distilled: b.p. 198-200° (17 mm), n_D^{20} 1.4460.

2. Methylene-bis-ethylmalonic ester. Two main fractions were got by vacuum distillation after reaction between methylene-bis-sodium malonic ester and ethyl bromide:

1st fraction [5.3 g (30.5%); b.p. 74-75° at 3 mm; n_D^{20} 1.4152], judging by its constants, was monoethylmalonic ester (literature data [10]: b.p. 77° at 5 mm), which was identified by transformation into ethylmalonic acid [**]

From the 2nd fraction (19 g; b.p. 164-175° at 3 mm) was isolated 8 g (22%) crystalline methylene-bis-ethylmalonic ester with m.p. 62-63° after recrystallization from dilute alcohol (literature data [4]: m.p. 61°).

To the non-crystallizing oil was added a few drops of ether; by this method it was possible to separate 1.2 g (7%) of the polymer of methylenemalonic ester with m.p. 154-156°, sparingly soluble in ether. The residue after removal of the ether was distilled in vacuum at 173-175° (5 mm), had n_D^{20} 1.4420, i.e. it was the original methylene-bis-malonic ester.

3. Methylene-bis-propylmalonic ester. Three fractions were collected, after two fractionations, from the product of reaction of methylene-bis-malonic ester with propyl bromide:

The 1st fraction [6.8 g (32.3%); b.p. 114-116° at 3 mm and n_D^{20} 1.4198] was propylmalonic ester. Literature data [12]: b.p. 222-227° (750 mm). Its hydrolysis gave a 70% yield of propylmalonic acid with m.p. 96° (from benzene). Literature data [13]: m.p. 96°.

Addition of ether to the 2nd fraction brought down 2.5 g polymer of methylene malonic ester with m.p. 154-155°. The residue after separation of the polymer was the original methylene-bis-malonic ester.

The 3rd fraction (17.0 g; b.p. 206-208° at 11 mm) crystallized completely; after recrystallization from aqueous alcohol, methylene-bis-propylmalonic ester was obtained with m.p. 41-42°. Yield 40% of the theoretical. Literature data [4]: m.p. 41-42°.

In this experiment, therefore, in contrast to the result of the experiment with ethyl bromide, it was possible to isolate the product of alkylation of the original methylene-bis-malonic ester by fractional distillation.

4. Methylene-bis-butylmalonic ester. Fractional distillation of the product of reaction between methylene-bis-malonic ester and butyl bromide gave 3 fractions:

The first fraction was monobutylmalonic ester, 6.6 g (30.0%):

B. p. 124-128° (18 mm); n_D^{20} 1.4229. Literature data [14]: b.p. 122° (12 mm); n_D^{20} 1.4222.

Addition of ether to the second fraction (6.2 g; b.p. 140-178° at 5 mm) brought down 2.7 g (15.0%) polymer of methylmalonic ester with m.p. 155-156°. The oil remaining after removal of the ether was the original methylene-bis-malonic ester (b.p. 174-175° at 5 mm; n_D^{20} 1.4420).

Redistillation of the third fraction (20.5 g; b.p. 185-205° at 5 mm) gave 14.0 g (37.4%) methylene-bis-butylmalonic ester in the form of a viscous oil with b.p. 198-199° at 5 mm; n_D^{20} 1.4522 (not described in the literature).

8.650 mg sub.: 19.672 mg CO_2; 6.932 mg H_2O. 4.540 mg sub.: 10.380 mg CO_2; 3.682 mg H_2O. Found %: C 62.00, 62.31; H 8.96, 9.16. $C_{23}H_{40}O_8$. Calculated %: C 62.13; H 9.06.

5. Methylene-bis-benzylmalonic ester. Two fractionations in vacuum of the product of reaction between methyllene-bis-malonic ester and benzyl chloride gave 4 fractions.

The first fraction (7.8 g) was unreacted benzyl chloride:

B. p. 54-55° (4 mm); n_D^{20} 1.5408.

From the 2nd fraction (7.8 g; b.p. 145-180° at 4 mm) was isolated 3.5 g (20%) polymer of methylenemalonic ester with m.p. 155-156°; the residue was unchanged methylene-bis-malonic ester with b.p. 172-175° (5 mm); n_D^{19} 1.4430.

[**] Hydrolysis of ethylmalonic ester was effected by heating for 3 hours with alcoholic KOH (0.4 g, 10 ml alcohol). The alcohol was driven off and the residue dissolved in water; after 3 extractions, the aqueous layer was acidified with hydrochloric acid; the ethylmalonic acid formed was extracted with ether and the ether was evaporated; the residual oil crystallized after standing for 3 days. Yield 0.5 g (70 %). After recrystallization from benzene the acid melted at 110-111°. Literature data [11]: m.p. 110-111°.

The third fraction (15 g; b.p. 210-240° at 4 mm) apparently contained, judging by the boiling point, dibenzylmalonic ester. Literature data [16]: b.p. 234° (23 mm).

Cooling of the 4th fraction (12.0 g; b.p. 240-250° at 4 mm) with solid carbon dioxide yielded 8.5 g (17%) crystals of methylene-bis-benzylmalonic ester with m.p. 44° after recrystallization from aqueous alcohol.

Methylene-bis-benzylmalonic ester had not previously been obtained in a crystalline form (literature data [4]: b.p. 200-250° in vacuum).

5.300 mg sub.: 13.175 mg CO_2; 3.410 mg H_2O. 5.965 mg sub.: 14.815 mg CO_2; 3.750 mg H_2O. Found %: C 67.83, 67.77 H 7.20, 7.03. $C_{29}H_{36}O_8$. Calculated %: C 67.95; H 7.02

6. Alkylation of methylene-bis-sodium malonic ester with secondary halides and with primary halides of branched structure (isopropyl, isobutyl and isoamyl bromide, also cyclohexyl chloride) did not lead to formation of normal products of reaction – methylene-bis-alkylmalonic esters. In all cases the main reaction was cleavage of the original methylene-bis-malonic ester: products isolated were the corresponding monoalkylmalonic esters, the crystalline polymer of methylenemalonic ester, and unreacted methylene-bis-malonic ester. The constants and yields of the monoalkylmalonic esters and the data in the literature are set forth in Table 1.

TABLE 1

Constants of monoalkylmalonic esters $RCH(COOC_2H_5)_2$

R	Boiling point	n_D^{20}	Yield (in % of theoretical)	Literature data	
				Boiling point	n_D^{20}
C_3H_7-iso	86-88° (5 mm)	1.4190	64.0	211-215° [15]	1.4180 [15]
C_4H_9-iso	101-103 (7 mm)	1.4282	64.7	118-120 (14 mm) [16]	–
C_5H_{11}-iso	133 135 (14 mm)	1.4243	58.3	160-165 (44 mm) [15]	1.4254 [15]
C_6H_{11}	134-136 (4 mm)	1.4340	18.1	163-165 (20 mm) [17]	–

Methylene-bis-5-alkylbarbituric acids

To sodium ethoxide (1.4 g sodium in 30 ml anhydrous alcohol) was added 2.4 g (0.04 mole) urea followed by 0.01 mole methylene-bis-alkylmalonic ester. The reaction mixture was heated on an oil bath at 120° for 18 hours, after which the alcohol was distilled off and the residue dissolved in water. The aqueous solution was extracted 3 times with ether and then acidified with concentrated hydrochloric acid until it had an acidic reaction. The precipitate which came down on cooling with ice and salt was filtered off and recrystallized from aqueous alcohol. All the prepared barbituric acids are poorly soluble in water and in organic solvents.

When preparing methylene-bis-5-alkylbarbituric acids containing butyl and benzyl radicals there was isolated an oil as well as the crystalline barbituric acids. This oil has not yet been investigated more closely.

The constants, yields and analytical data of the methylene-bis-5-alkylbarbituric acids and of methylene-bis-barbituric acid itself are set forth in Table 2 (see following page).

SUMMARY

1. The alkylation of methylene-bis-malonic ester with sodium ethoxide and alkyl halides was investigated.

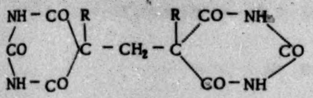
2. It was established that when employing in this reaction primary halides of normal structure, the yield of methylene-bis-alkylmalonic esters reached 40% of the theoretical, whereas when employing secondary halides or primary halides of branched structure the methylene-bis-alkylmalonic esters are not formed at all.

3. It was shown that the alkylation of methylene-bis-sodium malonic ester is accompanied by a secondary reaction involving cleavage, under the action of sodium ethoxide, of the intermediately formed sodium derivative of the monoalkylmethylene-bis-malonic ester; the products of this reaction are methylenemalonic ester (further transformed into a crystalline polymer) and monoalkylmalonic esters (yield from 11 to 40% when using primary halides of normal structure and 58-64% when using secondary bromides or primary ones with a branched structure).

4. Reaction of urea in presence of sodium ethoxide with the respective methylene-bis-alkylmalonic esters

TABLE 2

Methylene-bis-5-alkylbarbituric acids



Preparation number	R	Melting point	Yield (in % of theoretical)	N (in %)	
				Found	Calculated
1	H*	Decomposes without melting at about 300°	45.0	20.73 20.56	20.41
2	CH_3	252-253	44.8	18.40 18.50	18.9
3	C_2H_5	364-365 (with decomp.)	6.17	17.36 17.39	17.29
4	C_3H_7	358-359 (with decomp.)	56.2	15.83 15.77	15.89
5	C_4H_9	235-238	25.4	14.17 14.42	14.07
6	$C_6H_5CH_2$	210-211	15.3	12.37 12.78	12.49

* Gisling and Schwarzenbach [1] described the preparation of methylene-bis-barbituric acid (R = H) but did not give analytical data.

gave the previously undescribed methylene-bis-5-alkylbarbituric acids (alkyl methyl, ethyl, propyl and butyl; the benzyl radical can also be introduced in the same way)

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THE REACTION OF N-(2,5-DICHLOROPHENYL)-OXAZOLIDINE WITH FORMALDEHYDE

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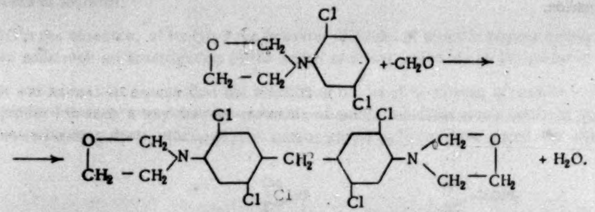
We have previously shown that 2,5-dichloroaniline, in contrast to aniline, does not react with ethylene oxide [1]. The apparent explanation of this difference in behavior is that the basic properties of 2,5-dichloroaniline are greatly weakened by the presence of a chlorine atom in the benzene ring, so that the amino group becomes non-reactive toward ethylene oxide.

In this connection it was of interest to establish whether the chlorine atoms in N-(2,5-dichlorophenyl)-oxazolidine which reacts with halogen-free N-phenyloxazolidine to form 4,4'-di-(oxazolidyl-N)-diphenylmethane, will react with formaldehyde. It should be noted that N-phenyloxazolidine reacts with formaldehyde with facility both in presence of hydrochloric acid[2] and of formic acid(experiment 2). It was found, however, that N-(2,5-dichlorophenyl)-oxazolidine does not react at all with formaldehyde in presence of formic acid, whereas in presence of hydrochloric acid condensation with formaldehyde takes place to give 4,4'-di(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane according to the scheme.



The structure of the product is confirmed by the determination of the nitrogen content and by the previous observation [2] that this type of condensation proceeds in the para-position. In this connection it should be emphasized that the above reaction scheme is not inconsistent with the generally accepted rule of substitution in the aromatic nucleus [3]. This is also supported by the fact that in the present instance reaction in the para-position is easier than in, say, the ortho-position since in the former position of the molecule of N-(2,5-dichlorophenyl)-oxazolidine there are no considerable steric barriers (remoteness of the oxazolidine ring from the para-position) which might have hindered the formation of 4,4'-di-(oxazolidyl-N)- 2,2', 5,5'-tetrachlorodiphenylmethane. Moreover, reaction of dialkylanilines usually procedd in the para-position [3].

EXPERIMENTAL

1. 4,4-Di-(oxazolidyl-N)-2,2',5,5'-tetrachloridphenylmethane. 54.5 g (0.25 mole) N-(2,5-dichlorophenyl)-oxazolidine, 12.3 g 36.7% formaldehyde (0.15 mole CH_2O), 70 ml alcohol and 1 ml hydrochloric acid (d 1.18) were stirred for 8 hours at room temperature. Heat was liberated at the start of the reaction and the temperature of the mass rose to 29°. At the conclusion of the stirring, the reaction mass was left overnight and the next day it was neutralized with sodium carbonate solution, when a white crystalline precipitate of 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane came down. The precipitate was filtered on a nutsch and washed with 80 ml alcohol and 250 ml water. The product was dried in the air. Yield 21 g (37.5%). After two recrystallizations from benzene, 4,4'-di-(oxazolidyl-N)-2,', 5,5'-tetrachlorodiphenylmethane melted at 154°

0.3320, 0.4263 g sub.: 15.14, 19.02 ml 0.1 N H_2SO_4. Found %: N 6.38, 6.24. $C_{19}H_{16}O_2N_2Cl_4$. Calculated %: N 6.25.

2. Preparation of 4,4'-di-(oxazolidyl-N)-diphenylmethane in presence of formic acid. 14.9 g N-Phenyloxazolidine, 4.9 g formaldehyde solution, 50 ml alcohol and 2 ml 70% formic acid were heated to 35-35° and stirred 8 hours. During the operation 4,4'-di-(oxazolidyl-N)-diphenylmethane gradually came down in the form of white scales. At the conclusion of the stirring the reaction mixture was left overnight. The next day the mixture was neutralized with sodium carbonate solution. The crystals of 4,4'-di-(oxazolidyl-N)-diphenylmethane were collected on a nutsch, washed with 50 ml alcohol, then with 500 ml water and finally with another 30 ml alcohol. The air-dried product melted at 138-140°.

Yield 10.3 g (66.5%). After recrystallization from benzene the m.p. was 141-142° in agreement with that reported in the literature for 4,4'-di-(oxazolidyl-N)-diphenylmethane [2].

SUMMARY

It was shown that N-(2,5-dichlorophenyl)-oxazolidine reacts with formaldehyde in presence of hydrochloric acid with formation of 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane. It was also established that in presence of formic acid N-(2,5-dichlorophenyl)-oxazolidine does not enter into reaction with formaldehyde, whereas the halogen-free N-phenyloxazolidine condenses with formaldehyde in presence of formic acid to give 4,4'-di-(oxazolidyl-N)-diphenylmethane.

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* T.p. = C. B. translation pagination.

ISOMERIZATION OF BICYCLIC TERPENE OXIDES DURING REACTION WITH ACETIC ANHYDRIDE

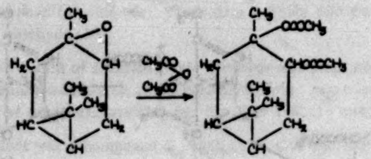
B. A. Arbuzov and Z. G. Isaeva

Researches by B. A. Arbuzov have established [1] that oxides of bicyclic terpene hydrocarbons – α-pinene, Δ^3-carene, β-pinene and camphene – undergo isomerization in various reactions. In the Grignard and Reformatsky reactions the oxides undergo preliminary isomerization to aldehydes: α-pinene oxide isomerizes to campholenaldehyde, β-pinene oxide to dihydromyrtenal, camphene oxide to camphenilanaldehyde, and Δ^3-carene oxide to an unsaturated aldehyde of uncertain structure. Isomerization of some of these oxides (oxides of α-pinene and Δ^3-carene) is accompanied by profound changes in their carbon skeleton. It was shown that the isomerizing agents during the Grignard and Reformatsky reactions are halides of magnesium and zinc.

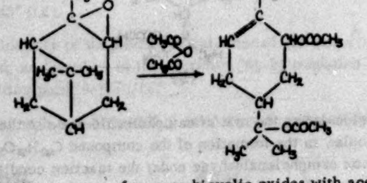
In 1949 we found [2] that the reaction of oxides of α-pinene, Δ^3-carene and camphene with alcohols in presence of sulfuric acid is likewise accompanied by isomerization of the oxides to aldehydes. The aldehydes react with the alcohols in presence of the sulfuric acid to form acetals. The action of alcohols on α-pinene oxide gives, apart from acetals, monoesters of sobrerol.

With the objective of studying the behavior of oxides of bicyclic terpene hydrocarbons in reactions without catalysts, we undertook an investigation of the action of acetic anhydride on the oxides of α-pinene, Δ^3-carene and camphene.

It was natural to assume that the reaction of oxides of α-pinene, Δ^3-carene and camphene with acetic anhydride would proceed in such a way that the molecule of acetic anhydride would combine with the oxide ring to form acetates of the corresponding diols: pinene glycol, carene glycol and camphene glycol. For example, with Δ^3 carene oxide:



Due to the circumstance, as reported in the literature, that α-pinene can isomerize even under mild conditions, its reaction with acetic anhydride might be expected to lead to sobrerol acetate (by analogy with the formation of sobrerol by the action of water on α-pinene oxide in presence of carbon dioxide [3]):



The experiments showed that the reaction of terpene bicyclic oxides with acetic anhydride is a complex process with formation of a mixture of products.

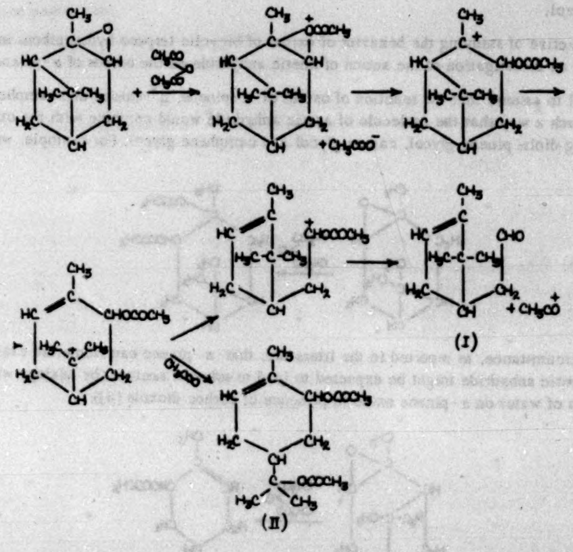
α-Pinene oxide

Three substances were isolated after reaction of α-pinene oxide with acetic anhydride. The constants of one of these substances with b.p. 58-64° (4 mm) were very similar to those campholenaldehyde (I) (see experimental). It was identified by preparation of the semicarbazone with m.p. 137-138°. The yield of campholenaldehyde in the reaction of α-pinene oxide with acetic anhydride was 20.4%.

The second reaction product with the composition $C_{12}H_{18}O_2$ (yield 30.2%) has b.p. 89-95° (6 mm). The compound gives an adduct with maleic anhydride with m.p. 142-144°. Hydrolysis of this compound with alkali in aqueous-alcoholic solution gave an alcohol with the composition $C_{10}H_{16}O$ and b.p. 75-81° (2.5 mm). The alcohol is esterified by boric acid; consequently, the hydroxyl group is not at the tertiary carbon atom. The compound $C_{12}H_{18}O_2$ is probably the acetate of the alcohol $C_{10}H_{16}O$ with conjugated double bonds. Its structure was not established.

The third reaction product is sobrerol diacetate (II): b.p. 125-128° (4 mm). Saponification of sobrerol acetate with 6% aqueous alkali solution gave sobrerol with m.p. 149-150°. There was no melting point depression in a mixed test with sobrerol prepared by hydration of α-pinene oxide in presence of acid. Yield of sobrerol acetate 26.1%.

In previous papers dealing with the rearrangements taking place on reaction of oxides of bicyclic terpenes with various reactants, we made use of a scheme in which was assumed the formation at an intermediate stage of an oxonium ion which later rearranged to a carbonium ion. Rearrangements of the carbonium ion would readily account for the formation of diverse products of reaction. Similar concepts explain the formation of the products of reaction with acetic anhydride of the oxide of α-pinene and, as will be shown later, of oxides of other bicyclic terpenes. Formation of the products of reaction of α-pinene oxide with acetic anhydride may be represented by the following scheme:



With the objective of elucidating the role of campholenaldehyde in the reaction of α-pinene oxide with acetic anhydride and, in particular, in the formation of the compound $C_{12}H_{18}O_2$, an experiment was performed on the action of acetic anhydride on campholenaldehyde under the reaction conditions (heating at 140° without a catalyst). Campholenaldehyde is unchanged under these conditions.

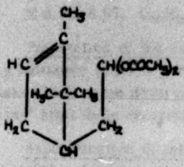
Reaction of acetic anhydride with campholenaldehyde in presence of sulfuric acid gave a crystalline substance with m.p. 70-72° whose analysis corresponded to $C_{14}H_{22}O_4$. Saponification of the compound with an aqueous-alcoholic solution of alkali gave campholenaldehyde (m.p. of semicarbazone 137-138°). Consequently, the compound with m.p. 70-72° is the diacetate with structure (III).

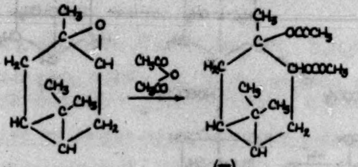
Δ^3-Carene Oxide

Δ^3-Carene oxide gives two products in reaction with acetic anhydride. 58.6 % of the carene oxide entered into the reaction, the remainder being recovered unchanged. As in the case of α-pinene oxide, a compound

$C_{12}H_{18}O_2$ with b.p. 86-88.5° (3 mm) was isolated. Yield 21.6%. This compound gives an adduct with maleic anhydride with m.p. 145-147°. A mixed test with the adduct of the analogous compound obtained by reaction of α-pinene oxide with acetic anhydride showed a depression, the mixed melting point being 117-120°. Saponification of the compound $C_{12}H_{18}O_2$ gives an alcohol $C_{10}H_{16}O$. As in the case of the product of reaction of α-pinene oxide with acetic anhydride, the structure of the compound $C_{12}H_{18}O_2$ was not established.

The second product of reaction of Δ^3-carene oxide with acetic anhydride was β-carene glycol diacetate (IV) with b.p. 120-121° (4 mm). Yield 7.7%. Saponification of this product gave β-carene glycol with m.p. 88-89°. Consequently, the reaction of Δ^3-carene with acetic anhydride proceeds partially with isomerization of Δ^3-carene oxide and in part normally.


(III)


(IV)

Camphene Oxide

The reaction of camphene oxide with acetic anhydride proceeds with complete isomerization of the oxide. In this process 38.3% of the camphene oxide isomerizes to camphenilanic aldehyde (V) which was identified by preparation of the semicarbazone with m.p. 191-192°. Among the reaction products was also found the compound $C_{12}H_{18}O_2$ with b.p. 93-95.5° (5 mm), n_D^{20} 1.4850, d_4^{20} 1.0043. Yield 20%. An aqueous-alcoholic solution of alkali saponifies the compound to camphenilanaldehyde. These data indicate that the compound is the acetate of the enolic form of camphenilanic aldehyde (VI).

The acetate of the enolic form of camphenilanic aldehyde was prepared by Semmler in 1909 [4] by the action of acetic anhydride and sodium acetate on camphenilanaldehyde. Semmler gave the following constants for the acetate of the enolic form of camphenilanaldehyde: b.p. 113-116° (10 mm), d_4^{20} 1.0125, n_D^{20} 1.4816.

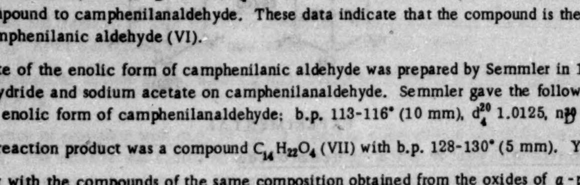
The third reaction product was a compound $C_{14}H_{22}O_4$ (VII) with b.p. 128-130° (5 mm). Yield 20.4%.

By analogy with the compounds of the same composition obtained from the oxides of α-pinene and Δ^3-carene it may be suggested that the action of acetic anhydride on camphene oxide also gives the acetate of a diol. Saponification with alkali gave a crystalline substance with m.p. 241-243° (VIII).

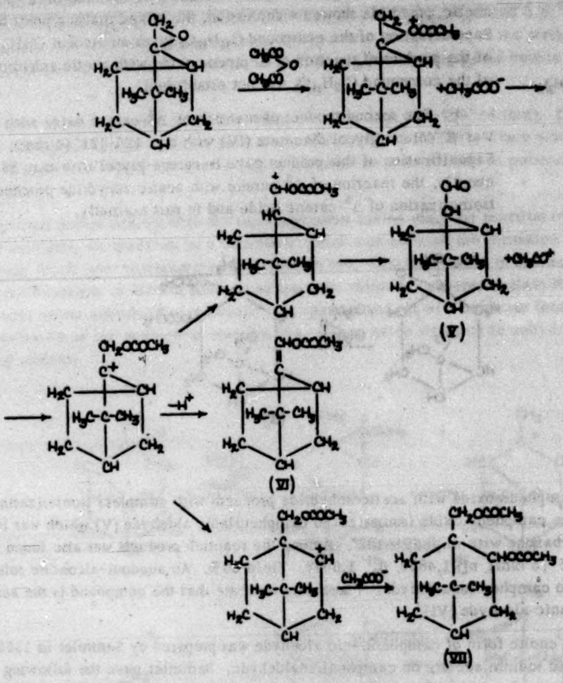
The crystalline compound was oxidized with potassium permanganate in a stream of carbon dioxide to form ketopinic acid with m.p. 232-233° (IX).

For confirmation of the identity of the product of oxidation of the diol with m.p. 241-243°, ketopinic acid with m.p. 230-232° was prepared, as described in the literature [5], by oxidation of bornyl chloride with nitric acid. A mixed test did not give a melting point depression.

Consequently, the product with b.p. 128-130° (5 mm) must be assigned the structure of the diacetate of 2,10-camphanediol (VII).


(VII) (VIII) (IX)

The mechanism of the reaction of camphene oxide with acetic anhydride may be represented by the following scheme:



EXPERIMENTAL

Action of acetic anhydride on α-pinene oxide

α-Pinene oxide was prepared by oxidation of α-pinene with peracetic acid; it had the constants: b.p. 67-67.5° (12 mm), d_4^{20} 0.9601, n_D^{20} 1.4693.

1st experiment. Reactants were 96.8 g pinene oxide and 151 g acetic anhydride. The α-pinene oxide was run dropwise into the boiling acetic anhydride in the course of 1½ hours. Then the reaction mixture was boiled 4½ hours (temperature in the reaction mixture 140-143°). The acetic anhydride was distilled off in vacuum; fractionation of the residue in a Widmer column yielded three fractions:

1st – b.p. 58-64° (4 mm), 19.7 g, d_4^{20} 0.9172, n_D^{20} 1.4650; 2nd – b.p. 89-95° (6 mm), 29.9 g, d_4^{20} 0.9759, n_D^{20} 1.4802; 3rd – b.p. 125-128° (4 mm), 33.6 g, d_4^{20} 1.0456, n_D^{20} 1.4668.

2nd experiment. Reactants were 86.5 g α-pinene oxide and 257 g acetic anhydride. The α-pinene oxide was run into the acetic anhydride, heated to 130°, in the course of 45 minutes. After running in ¼ of the amount of α-pinene oxide, the reaction mixture boiled. After all had been run in, the reaction mixture was boiled for another 40 minutes. The mixture was worked up as described for the 1st experiment, and also gave three fractions:

1st – b.p. 66-71° (5 mm), 22.2 g, d_4^{20} 0.9187, n_D^{20} 1.4668; 2nd – b.p. 94-100° (4.5 mm), 20.9 g, d_4^{20} 0.9756, n_D^{20} 1.4805; 3rd – b.p. 134-136° (4 mm), 29 g, d_4^{20} 1.0462, n_D^{20} 1.4685.

Preparation of the semicarbazone of campholenaldehyde. Semicarbazide hydrochloride (1.1 g) and sodium acetate (1.5 g) were dissolved in a little water and into the solution was run the compound (1.1 g) with b.p. 58-64° (4 mm). Shaking of the mixture for 20-25 minutes resulted in separation of a solid; weight 1.3 g after washing with water and pressing on filter paper. After two recrystallizations from ethyl alcohol the m.p. of the semicarbazone was 137-138°. The m.p. of campholenaldehyde semicarbazone was 138-139°. The mixed melting point was 137-138°.

Examination of substance with b.p. 89-95° (6 mm)

d_4^{20} 0.9759, n_D^{20} 1.4802, MR_D 56.49. $C_{12}H_{18}O_2F_2$. Calculated 56.14.

0.0966, 0.1000 g substance: 0.2602, 0.2692 g CO_2; 0.0778, 0.0808 g H_2O. Found %: C 73.45, 73.42; H 8.95, 8.97. $C_{12}H_{18}O_2$. Calculated %: C 74.18; H 9.35.

Preparation of the adduct of the substance with b.p. 89-95° (6 mm) with maleic anhydride. A mixture of 3 g substance and 1.6 g maleic anhydride was heated on a water bath at 80-85° for 6 hours. The small precipitate which came down on cooling was filtered off. Crystals came down from the filtrate on standing; m.p. 142-144° after three recrystallizations from alcohol. The adduct is readily soluble in alcohol.

Saponification of substance with b.p. 89-95° (6 mm) with aqueous-alcoholic NaOH. Into a solution of 1.7 g NaOH in 11 ml water and 21 ml alcohol was run 8 g substance. The color of the mixture became light-brown. The color changed to reddish-brown on heating at 40-45° for 5 hours. The reaction mixture was then diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The residue after driving off the ether and alcohol was vacuum-distilled:

b.p. 75-81° (2.5 mm), 4.5 g, d_4^{20} 0.9648, n_D^{20} 1.5010, MR_D 46.41. $C_{10}H_{16}OF_2$. Calculated 46.77.

0.0880 g substance: 0. 2542 g CO_2; 0.0818 g H_2O. 0.1116 g substance: 16.8 ml CH_4 (14°, 758 mm). Found %: C 78.78; H 10.32; OH 10.88. $C_{10}H_{16}O$. Calculated %: C 78.89; H 10.59; OH 11.18.

Action of acetic anhydride on campholenaldehyde in presence of sulfuric acid

Reactants were 10 g campholenaldehyde [b.p. 76-82° (9 mm), d_4^{20} 0.9215, n_D^{20} 1.4650], 35 g freshly distilled acetic anhydride and 1 drop sulfuric acid (d 1.84). The campholenaldehyde was run dropwise into the acetic anhydride containing the sulfuric acid. No heating of the mixture was detected. The reaction mixture was heated on a water bath at 65° for 1 hour and then neutralized with sodium acetate. The residue after removal of the acetic anhydride was distilled in vacuum in a Widmer column to give three fractions:

1st – b.p. 75-80° (3 mm), 2 g, n_D^{20} 1.4730; 2nd – b.p. 80-90° (3 mm), 1.7 g, d_4^{20} 0.9870, n_D^{20} 1.4672; 3rd – b.p. 90-120° (3 mm), 3.3 g, n_D^{20} 1.4697.

The 2nd and 3rd fractions at once started to crystallize. The crystals were filtered off, and pressed on filter paper; weight 3.2 g. After 3 recrystallizations from alcohol the m.p. was 70-72°.

0.1240 g substance: 0.2990 g CO_2; 0.0972 g H_2O. Found %: C 65.76; H 8.71. $C_{14}H_{22}O_4$. Calculated %: C 66.11; H 8.72.

Saponification of substance with m.p. 70-72°. 1 g substance was treated with 0.5 g NaOH in 10 ml water and 10 ml ethanol. The mixture was heated on a water bath at 90-100° for 6 hours. The reaction mixture was diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The ether was distilled off; from the residue was obtained campholenaldehyde semicarbazone with m.p. 137-138°.

Examination of substance with b.p. 125-128° (4 mm)

d_4^{20} 1.0456, n_D^{20} 1.4668, MR_D 67.38, $C_{14}H_{22}O_4$. Calculated 67.49.

0.1332 g substance: 0.3214 g CO_2; 0.1030 g H_2O. Found %: C 65.81; H 8.58. $C_{14}H_{22}O_4$. Calculated %: C 66.1; H 8.72.

Saponification of substance with b.p. 125-128° (4 mm). A mixture of 4 g substance, 2 g NaOH and 32 ml water was shaken at room temperature for 70 hours. The precipitated crystals were filtered and washed with ether. M.p. 147-149°. After recrystallization from alcohol the m.p. was 149-150° (sobrerol has m.p. 150°). A mixed test with the sobrerol prepared by hydration of α-pinene oxide in presence of acid melted at 148-150°.

Action of acetic anhydride on Δ^3-carene oxide

Reactants were 70 g Δ^3-carene oxide [b.p. 72-74° (10.5 mm) d_4^{20} 0.9475, n_D^{20} 1.4680] and 190 g freshly distilled acetic anhydride. The Δ^3-carene oxide was run into the boiling acetic anhydride in the course of 2 hours 40 minutes; the solution was then boiled for another 4 hours. Three fractions were collected on fractionation of the mixture:

1st – b.p. 51-54 (4 mm), 29 g, d_4^{20} 0.9480; n_D^{20} 1.4690; 2nd – b.p. 86-88.5° (3 mm), 11.3 g, d_4^{20} 0.9802, n_D^{20} 1.4790; 3rd – b.p. 120-121° (4 mm), 5.3 g, d_4^{20} 1.0455, n_D^{20} 1.4670.

Examination of substance with b.p. 86-88.5° (3 mm)

d_4^{20} 0.9802, n_D^{20} 1.4790, MR_D 56.12. $C_{12}H_{18}O_2{}^{F}{}_{2}$.Calculated 56.14.

0.1196 g sub.: 0.3252 g CO_2; 0.1000 g H_2O. Found %: C 74.15; H 9.29, $C_{12}H_{18}O_2$.Calc. %: C 74.18; H 9.35.

Preparation of adduct with b.p. 86-88.5° (3 mm) with maleic anhydride. A mixture of 2.9 g substance and 1.6 g maleic anhydride was heated on a water bath at 50° until the maleic anhydride had dissolved. On standing, crystals came down which were filtered off, washed with ether, and recrystallized from alcohol; m.p. 145-146°. The melting point after boiling with ligroine was 145-147°.

Saponification of substance with b.p. 86-88.5° (3 mm). Reactants were 4.5 g substance and 1.8 g KOH in 8 ml water and 15 ml ethanol. On mixing the reactants a dark-brown color was imparted to the mixture and a still darker color was acquired after heating on a water bath at 40-45° for 5 hours. The mixture was then diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The residue after driving off the ether and alcohol was distilled to give 1.9 g substance with b.p. 75.5-77° (2.5 mm).

d_4^{20} 0.9636 n_D^{20} 1.4964, MR_D 46.12. $C_{10}H_{16}O\bar{F}_2$. Calculated 46.77.

0.1283 g sub.: 20.61 ml CH_4 (20°, 760 mm). Found %: OH 11.39.$C_{10}H_{16}O$. Calculated %: OH 11.18.

Examination of substance with b.p. 120-121° (4 mm)

d_4^{20}1.0455, n_D^{20} 1.4670, MR_D 67.41. $C_{14}H_{22}$ O. Calculated 66.46.

0.0930 g sub.: 0.2260 g CO_2; 0.0716 g H_2O. Found %: C 66.27; H 8.55 $C_{14}H_{22}O_4$. Calculated %: C 66.11; H 8.72.

Saponification of substance with b.p. 120-121° (4 mm). A mixture of 1.5 g substance, 1.2 g NaOH and 19 ml water was shaken 17 hours at room temperature. The resultant crystals were filtered off, washed with ether and recrystallized three times from ligroine; m.p. 88-89°. Melting point of anhydrous β-carene glycol 89-90°. A mixed test with β-carene glycol prepared by hydration of Δ^3-carene oxide in persence of hydrochloric acid (m.p. after two two recrystallizations from ligroine 88-89°) gave a melting point of 87-89°.

Action of acetic anhydride on camphene oxide

Reactants were 50.4 g camphene oxide and 136 g acetic anhydride. The solution of camphene oxide in acetic anhydride was heated on a water bath for 3 hours and then boiled for 7 hours. Repeated fractionations of the reaction mixture in a Widmer column gave three fractions.

1st - b.p. 80-87° (9.5 mm) 19.3 g (crystallizes on distillation); 2nd b.p.93-95.5°. (5 mm) 7.9 g d_4^{20} 1.0043, n_D^{20} 1.4850; 3rd b.p. 128-130°. (5 mm), 10.6 g, d_4^{20}1.072, n_D^{20} 1.4718.

Preparation of semicarbazone of camphenilanaldehyde

To a saturated solution of 1 g semicarbazide hydrochloride and 1.5 g sodium acetate in water was added 1 g substance with b.p. 80.87° (9.5 mm). The mixture was diluted with methanol until the substance dissolved. On shaking for 2-3 minutes the solution deposited a white precipitate which was filtered off, washed with water and pressed on filter paper. Recrystallization from ethanol gave fine crystals with m.p. 191-192°. No change of m.p. after a second recrystallization. The semicarbazone of the camphenilanaldehyde prepared by isomerization of camphene oxide with zinc bromide had m.p. 191-192° [1]. A mixed sample melted at 190-192°.

Examination of substance with b.p. 93-95,5 [illegible] (5 mm).

d_4^{20} 1.0043, n_D^{20} 1.4850, MR_D 55.36 $C_{12}H_{18}O_2{}^{F}$. Calculated [illegible].

0.1254 g sub.: 0.3412 g CO_2; 0.1022 g H_2O. Found %: 74.20 [illegible] 9.06. $C_{12}H_{18}O_2$. Calculated %: C 74.18. H 9.35.

Saponification of substance with b.p. 93-95.5° (5 mm). A mixture of 4.1 g substance, 1.3 g KOH, 6 ml water and 14 ml ethanol was heated on a water bath for 12 hours at 80-85°, after which it was diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The residue after removal of the ether and alcohol was distilled to give a fraction with:

B.p. 65-72° (3 mm) 1.6 g, d_4^{20}1.0087, n_D^{20} 1.4848.

Crystallization commenced even during distillation. The crystals were filtered off and pressed on filter paper; a semicarbazone was prepared from them.

Preparation of semicarbazone of camphenilanaldehyde. Reactants were 0.2 g substance, 0.3 g semicarbazide and 0.4 g sodium acetate. To the mixture was added methanol until the aldehyde dissolved. On shaking, a precipitate came down; weight of crude semicarbazone 0.1 g. M.p.189-190° after two recrystallizations from alcohol. A mixture with the semicarbazone of camphenilanaldehyde prepared by isomerization of camphene oxide in the reaction with acetic anhydried melted at 189-190°.

Examination of substance with b.p. 128-130° (5 mm)

d_4^{20} 1.072, n_D^{20} 1.4718, MR_D 66.33. $C_{14}H_{22}O_4$. Calculated 65.76.

0.0950 g sub.: 0.2298 g CO_2; 0.0732 g H_2O. Found %: C 65.97; H 8.56. $C_{14}H_{22}O_4$. Calculated %: 66.11; H 8.72.

Saponification of substance with b.p. 128-130° (5 mm). 6 g substance was treated with 2.5 g NaOH in 15 ml water and 15 ml alcohol. The mixture was heated on a water bath 8 hours at 40-50°. The reaction mixture was diluted with water and extracted with ether. The residue after removal of the ether became viscous but did not crystallize. On dilution with ligroine a crystalline product separated. Recrystallization from ligroine gave 1.2 g substance with m.p. 238-242°; after recrystallization the m.p. was 241-243°. The melting point was unchanged after a third recrystallization.

0.0578 g sub.: 01493 g CO_2; 0.0560 g H_2O. Found %: C 70.45; H 10.76. $C_{10}H_{18}O_2$. Calculated %: C 70.54 H 10.65.

Oxidation of substance with m.p. 241-243°. 1.2 g substance was dissolved in 120 ml water with heating. To the solution, cooled to 20°, was added with stirring a solution of 2.4 g $KMnO_4$ in 60 ml water. Oxidation was effected in a stream of carbon dioxide. After two days' standing the reaction mixture was steam-distilled and 250 ml solution came over and was extracted with ether prior to evaporation. After concentration to a volume of 10 ml, the solution was acidified with hydrochloric acid and extracted with ether. The residue after removal of the ether crystallized completely on standing. After two recrystallizations from ligroine the m.p. was 232-233°.

Oxidation of bornyl chloride with nitric acid. 13 g bornyl chloride was treated with 23.9g 94% nitric acid. The bornyl chloride was introduced into the nitric acid in small portions while cooling with water. Reaction was conducted at a temperature not higher than 24°. After standing at room temperature for 30 hours, the reaction mixture was neutralized with milk of lime and the solution filtered. The filtrate was saturated with carbon dioxide and again filtered before evaporation to a small volume; it was then acidified with hydrochloric acid and extracted with ether. After removal of the ether, the residue crystallized; weight 1.8 g . M. p. 230-232° after recrystallization from water. A mixture with the acid prepared by oxidation of the diol with m.p. 241-243° melted at 230-232.5°

SUMMARY

1. A study was made of the reaction of α -pinene oxide, Δ^3-carene oxide and camphene oxide with acetic anhydride.

2. In this reaction α -pinene oxide yielded campholenaldehyde. sobrerol diacetate and the acetate of a dienic alcohol of unclarified structure.

3. Reaction of Δ^3-carene oxide with acetic anhydride gave β -carene glycol diacetate and the acetate of a dienic alcohol of unknown structure.

4. Camphene oxide with acetic anhydride forms camphenilanaldehyde, the acetate of the enolic form of camphenilanaldehyde and 2,10-camphanediol acetate.

5. A mechanism is advanced for the formation of diverse reaction products which assumes rearrangement to the carbonium ion.

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* T.p. = Consultants Bureau Translation pagination.

SYNTHESIS OF ORGANOANTIMONY COMPOUNDS OF THE TYPE OF Ar_2SbX_3 and Ar_3SbX_2 VIA THE DOUBLE DIAZONIUM SALTS OF ANTIMONY PENTACHLORIDE

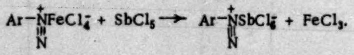
O. A. Reutov and V. V. Kondratyeva

Double diazonium salts of antimony trichloride (May salts), prepared more than 40 years ago [1], have found wide application for synthesis of diverse aromatic organoantimony compounds. Unlike the May salts, the double diazonium salts of antimony pentachloride were entirely unkown, since their preparation even in a strongly acidic aqueous medium is hindered by the facility of hydrolysis of $SbCl_5$, and the employment of organic hydroxyl-free solvents is prevented by the poor solubility in the latter of aryldiazonium chlorides.

Their synthesis has been effected by utilizing the exchange reaction (discovered by one of us [2]) between double diazonium salts of ferric chloride and chlorides of other heavy metals:

$$ArN_2Cl \cdot FeCl_3 + MeCl_n \rightarrow ArN_2Cl \cdot MeCl_n + FeCl_3.$$

On running a solution of antimony pentachloride in chloroform or carbon tetrachloride into an acetone solution of $ArN_2Cl \cdot FeCl_3$ and then stirring in ether, the double diazonium salt of antimony pentachloride comes down:



$$Ar-\underset{\underset{N}{|||}}{\overset{+}{N}}FeCl_4^- + SbCl_5 \rightarrow Ar-\underset{\underset{N}{|||}}{\overset{+}{N}}SbCl_6^- + FeCl_3.$$

The double salts synthesized by this reaction are set forth in Table 1.

The double diazonium salts of antimony pentachloride proved to be a convenient starting point for synthesis of organoantimony compounds of the type of Ar_2SbX_3 and $Ar_3\,SbX_2$. Their decomposition by iron powder in an acetone medium proceeds according to two equations:

$$2\,ArN_2Cl \cdot SbCl_5 + 3Fe \rightarrow Ar_2SbCl_3 + 2N_2 + SbCl_3 + 3FeCl_2. \qquad (I)$$

$$3ArN_2Cl \cdot SbCl_5 + 5Fe \rightarrow Ar_3SbCl_2 + 3N_2 + 2SbCl_3 + 5FeCl_2. \qquad (II)$$

The results of decompositon of various double diazonium salts of antimony pentachloride by iron powder are set forth in Table 2.

As we see from the data of Table 2, only one of the above reactions takes place in most cases, and (usually in high yield) only one type of organoantimony compound is formed.

EXPERIMENTAL

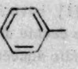
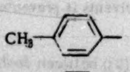
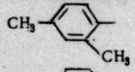
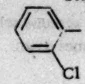
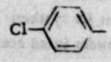
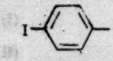
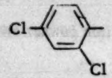
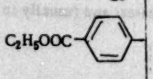
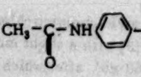
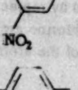
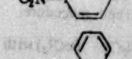
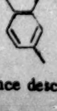
Preparation of dobule diazonium salts of ferric chloride. Preparation of the double salts of aryldiazonium chlorides ($ArN_2Cl \cdot FeCl_3$) was effected under the conditions described by Kocheshkov and Nesmeyanov [3] with a slight modification consisting in dissolving the ferric chloride in the minimum amount of water heated to 50-60°, after which the solution was cooled to -5°. The cooled solution of ferric chloride was run into a cooled solution of the diazotized amine, after which the double salt of aryldiazonium chloride and ferric chloride was precipitated by addition with stirring of concentrated hydrochloric acid. By this procedure intense cooling is not required. Precipitation of the double salt proceeds readily even at temperatures of 0 to +5°. The prepared salts can (if necessary) be purified by reprecipitation with ether from acetone solution. The pure, dry double salts of aryldiazonium chlorides and ferric chloride are fairly stable and they can be stored in the air for periods of 2-3 days to 2 weeks (depending upon the nature of the aromatic radical) without appreciable decompositon.

The following double diazonium salts were synthesized for the first time by the above-described procedure:

Double salt of ferric chloride and p-carbethoxyphenyldiazonium chloride ($p\text{-}C_2H_5OOCC_6H_4N_2Cl \cdot FeCl_3$) with m.p. 72-73° (decomp.), greyish-yellow color: yield 88 %.

TABLE 2

Substances formed by decomposition of double diazonium salts of antimony pentachloride $ArN_2Cl \cdot SbCl_5$ by iron powder in acetone

Ar–	Ar_2SbX_3						
	Formula	Yield (in %)	in the form of which compound it is identified	melting point	color	results	
						C	
						calculated	found
	$(C_6H_5)_2SbOOH$	67	$(C_6H_5)_2SbCl_3$	171-172°	white	31.06	31.42 31.36
	$(CH_3C_6H_4)_2SbOOH$	58	$(CH_3C_6H_4)_2SbCl_3$	155	white	40.95	41.02 41.10
				Not formed			
				Not formed			
	$(ClC_6H_4)_2SbOOH$	59	$(ClC_6H_4)_2SbCl_3$	149-150	white	31.92	31.68 31.83
	$(IC_6H_4)_2SbOOH$	81	$(IC_6H_4)_2SbOCl$*	149	white	–	–
				Not formed			
				Not formed			
				Not formed			
	$(O_2NC_6H_4)_2SbOOH$	72	$(O_2NC_6H_4)_2SbCl_3$	182-185	white	30.50	30.37 30.43
	$(O_2NC_6H_4)_2SbOOH$	88	$(O_2NC_6H_4)_2SbCl_3$	190 (contracts)	white	30.50	30.28 30.36
				Not formed			

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* Substance described for first time.

of analysis (in %)				Ar$_3$SbX$_2$									
H		Sb		Formula	melting point	color	Yield (in %)	results of analysis (in %)					
								C		H		Sb	
calculated	found	calculated	found					calculated	found	calculated	found	calculated	found
2.61	2.83 2.92	–	–	Not formed									
3.44	3.21 3.43	–	–	$(CH_3C_6H_4)_3SbCl_2$	156°	white	29	–	–	–	–	–	–
				$[(CH_3)_2C_6H_3]_3SbCl_2$	190.5-191.5	white	52	56.71	57.03 57.01	5.39	5.48 5.55	–	–
				$(ClC_6H_4)_3SbCl_2$	205-206	white	73	40.97	40.91 40.82	2.30	2.25 2.18		
1.79	1.72 1.85	–	–	$(ClC_6H_4)SbCl_2$	193	white	30	40.97	41.05 40.97	2.30	2.36 2.55	–	–
–	–	21.02	21.03 21.15	Not formed									
				$(Cl_2C_6H_3)_3SbCl_2$*	235	white	60	–	–	–	–	19.30	19.00 19.20
				$(C_2H_5OOCC_6H_4)_3SbCl_2$	133-134	white	20	50.63	50.86 50.91	4.24	4.08 4.17	–	–
				$(CH_3CONHC_6H_4)_3SbCl_2$	170 (sintering)	white	76	48.42	48.34 48.20	4.07	3.98 3.89		
1.71	1.52 1.67			Not formed									
1.71	1.78 1.64	–	–	Not formed									
				$(C_{10}H_7)_3SbCl_2$*	158-168	white	79	62.74	62.43 62.54	3.69	3.87 3.82	–	–

TABLE 1

Double Diazonium Salts of Antimony Pentachloride.

Formula	M.p. (with decomp.)	Solubility					Color	Yield (in %)	Results of analysis (in %)							
									C		H		N		Sb	
		acetone	alcohol	ether	benzene	water			Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$C_6H_5N_2Cl \cdot SbCl_5$	66-67°	5	4	1	2	1	White with yellowish tinge	86	16.39	16.04 16.91	1.15	1.56 1.42	6.37	6.38 6.56	-	-
p-$CH_3C_6H_4N_2Cl \cdot SbCl_5$	107-107.5	5	4	1	2	1	White	85	18.52	18.68 18.46	1.55	1.52 1.57	6.17	6.67 6.59	-	-
o-$ClC_6H_4N_2Cl \cdot SbCl_5$	139	5	4	1	2	1	White	85	15.29	15.26 15.39	0.85	1.17 1.02	5.91	6.16	-	-
p-$ClC_6H_4N_2Cl \cdot SbCl_5$	144	5	4	2	1	1	White	89	-	-	-	-	5.91	6.32 6.48	-	-
p-$BrC_6H_4N_2Cl \cdot SbCl_5$	165-167	5	4	2	1	1	White	65	-	-	-	-	5.40	5.33 5.36	-	-
p-$YC_6H_4N_2Cl \cdot SbCl_5$	123-124	5	4	1	1	1	Light-yellow	89	-	-	-	-	4.95	4.81 4.65	-	-
2,4-$Cl_2C_6H_3N_2Cl \cdot SbCl_5$	155	5	4	1	1	1	White	84	-	-	-	-	-	-	24.00	24.24 24.12
2,4,6-$Br_3C_6H_2N_2Cl \cdot SbCl_5$	223	5	3	1	1	1	White	92	-	-	-	-	-	-	18.60	18.77 18.72
p-$C_2H_5OOCC_6H_4N_2Cl \cdot SbCl_5$	104-105	5	2	1	1	1	White	93	-	-	-	-	-	-	23.80	23.90 23.95
p-$(CH_3)_2NC_6H_4N_2Cl \cdot SbCl_5$	143	5	2	1	1	1	Orange	89	-	-	-	-	-	-	25.23	25.51 25.32
p-$CH_3CONHC_6H_4N_2Cl \cdot SbCl_5$	143-145	5	3	1	1	1	White	94	-	-	-	-	-	-	29.67	29.98 29.76
o-$O_2NC_6H_4N_2Cl \cdot SbCl_5$	149-150	5	4	1	2	1	White with yellowish tinge	34	-	-	-	-	8.67	8.98 8.78	-	-
m-$O_2NC_6H_4N_2Cl \cdot SbCl_5$	141-142	5	4	1	2	1	White	77	-	-	-	-	8.67	8.80 8.76	- -	- -
p-$O_2NC_6H_4N_2Cl \cdot SbCl_5$	114-115	5	4	1	2	1	White with yellowish tinge	75	-	-	-	-	8.67	8.57 8.63	-	-
α-$C_{10}H_7N_2Cl \cdot SbCl_5$	77-78	4	3	1	1	1	Yellow-green	79	-	-	-	-	5.72	5.82 5.77	-	-
β-$C_{10}H_7N_2Cl \cdot SbCl_5$	92	4	3	1	1	1	Canary-yellow	65	24.51	24.56	1.44	1.58 1.50	5.72	5.90 5.84	-	-
2,4-$(CH_3)_2C_6H_3N_2Cl.SbCl_5$	78-78.5	5	2	1	1	1	White	49	-	-	-		5.99	6.34 6.42	-	-
p-p'-$Cl_5Sb.ClN_2C_6H_4-C_6H_4N_2Cl \cdot SbC_5$	125-126	4	3	1	1	2	Yellowish	76	-	-	-	-	6.38	6.72 6.60	-	-

Double salt of ferric chloride and p-dimethylaminophenyldiazonium chloride $[p\text{-}(CH_3)_2NC_6H_4N_2Cl \cdot FeCl_3]$ with m.p. 109° (decomp.), yellow color; yield 87%.

Double salt of ferric chloride and p-acetylaminophenyldiazonium chloride $(p\text{-}CH_3CONHC_6H_4N_2Cl \cdot FeCl_3)$ with m.p. 109° (decomp.), yellow color; yield 80%.

Double salt of ferric chloride and m-xylyldiazonium chloride $[2,4\text{-}(CH_3)_2C_6H_3N_2Cl \cdot FeCl_3]$ with m.p. 45-46° (decomp.), light yellow-color; yield 80%.

Double salt of ferric chloride and 2,4-dichlorophenyldiazonium chloride $(2,4\text{-}Cl_2C_6H_3N_2Cl \cdot FeCl_3)$ with m.p. 132° (decomp.), light yellow color; yield 89%.

Double salt of ferric chloride and 2,4,6-tribromophenyldiazonium chloride $(2,4,6\text{-}Br_3C_6H_2N_2Cl \cdot FeCl_3)$ with m.p. 126° (decomp.), yellow color; yield 63%.

Double salt of ferric chloride and α-naphthyldiazonium chloride $(\alpha\text{-}C_{10}H_7N_2Cl \cdot FeCl_3)$ with m.p. 75-77° yellow color; yield 73%.

Double salt of ferric chloride and β-naphthyldiazonium chloride $[\beta\text{-}C_{10}H_7N_2Cl \cdot FeCl_3]$ With m.p. 78-79° (decomp.), yellow color; yield 87%.

Double salt of ferric chloride and diazotized benzidine $(p,p'\text{-}Cl_3Fe \cdot ClN_2C_6H_4\text{—}C_6H_4N_2Cl \cdot FeCl_3)$, decomposes with explosion at 97-98°, yellow color, yield 86%.

Preparation of double diazonium salts of antimony pentachloride. 0.05 mole double salt of ferric chloride and aryldiazonium chloride was dissolved in the cold in the minimum amount of dry aceton. To the solution was added (with cooling with snow and salt and with stirring) a solution 18 g (0.06 mole) antimony pentachloride in 75 ml cold, dry chloroform. To the resultant crystal magma with continued stirring was added 200 ml ether. The precipitate of double salt $ArN_2Cl \cdot SbCl_5$ was filtered off, washed with ether and dried in the air. The double diazonium salts of antimony pentachloride can be obtained in the analytically pure form by reprecipitation in the cold with ether from aceton solution. They can be stored in the air without appreciable decomposition for 1-2 weeks to 2-4 months depending upon the nature of the aromatic radical. The double diazonium salts of antimony pentachloride synthesized by this procedure are set forth in Table 1.

Decomposition of double diazonium salts of antimony pentachloride with iron powder. To a suspension of 5.6g (0.1 g-atom) iron powder, passed through a 100-mesh screen, in 50 ml dry aceton was added a solution of 0.025 mole double salt of antimony pentachloride and aryldiazonium chloride in 40 ml dry acetone with good mechanical stirring in the course of 15 minutes. The first third of the solution was run in a single portion; 5 minutes later, when vigorous evolution of nitrogen had started and the reaction mixture had heated up, the remainder of the solution was run in at such rate that a continuous vigorous stream of gas was coming off. After the whole of the solution had been run in, the mixture was stirred for another 1/2 hour.

The inorganic precipitate was filtered off and the solvent distilled off from the filtrate in vacuum in the cold. To the residue (brown oil), after washing with 5 N hydrochloric acid (20 and 15 ml), was added 30 ml cold 96% alcohol with stirring. The insoluble triarylantimony dichloride was filtered off and recrystallized from a suitable solvent.

The alcoholic filtrate (after separation of the triarylantimony dichloride) was poured into cooled 5% ammonia solution. The gelatinous precipitate of diarylstibinic acid was filtered off, well washed with water and dried in the air. The acid was identified by conversion to diarylantimony trichloride by heating with 5N hydrochloric acid.

SUMMARY

1. A method was developed for synthesis of previously unknown double diazonium salts of antimony pentachloride.

2. A method was evolved for synthesis of organoantimony compounds of the type of Ar_2SbX_3 and Ar_3SbX_2 via the double diazonium salts of antimony pentachloride.

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Double salt of ferric chloride and [illegible] ([illegible]), yellow color; [illegible].

Double salt of ferric chloride and [illegible] [illegible] (decomp.), yellow color; yield [illegible].

Double salt of ferric chloride and m-[illegible] [illegible] (decomp.), light yellow color; yield [illegible].

Double salt of ferric chloride and [illegible] [illegible] (decomp.), light yellow color; yield [illegible].

Double salt of ferric chloride and [illegible] [illegible] (decomp.), yellow color; yield [illegible].

Double salt of ferric chloride and o-[illegible] [illegible] yellow color; yield [illegible].

Double salt of ferric chloride and [illegible] [illegible] (decomp.), yellow color; yield [illegible].

Double salt of ferric chloride and [illegible] [illegible] decomposes with explosion at [illegible], yellow color; yield [illegible].

Preparation of double diazonium salts of antimony pentachloride. [illegible] double salt of ferric chloride and [illegible] chloride was dissolved in the [illegible] amount of dry acetone. To the solution was added [illegible] [illegible] and [illegible] with stirring a solution of [illegible] antimony pentachloride in [illegible] dry [illegible]. To the resultant [illegible] with continued stirring [illegible] the [illegible] of [illegible] [illegible], was [illegible] off, washed with ether and dried in the air. The double diazonium salts of antimony pentachloride can be [illegible] [illegible] [illegible] in [illegible] [illegible] other than [illegible] [illegible]. They can be stored in the air without appreciable decomposition [illegible] [illegible] the nature of the aromatic radical. The double diazonium salts of antimony pentachloride [illegible] are [illegible] in Table 1.

The [illegible] of double diazonium salts of antimony pentachloride with iron powder. To a suspension of [illegible] g ([illegible] g-atom) iron powder, passed through a [illegible] mesh screen, in [illegible] ml dry acetone was added a solution of [illegible] double salt of antimony pentachloride and [illegible] chloride in [illegible] ml dry acetone with good mechanical stirring [illegible] of [illegible] minutes. The first third of the solution was [illegible] in a single portion [illegible] evolution of nitrogen had started and the reaction mixture had [illegible] the remainder of the solution was run in at [illegible] that a continuous [illegible] stream of gas was [illegible]. After the whole of the solution had been run in, the mixture was stirred for another 1/2 hour.

The inorganic precipitate was filtered off and the solvent distilled off from the filtrate [illegible]. To the residue (brown oil), after [illegible] with [illegible] [illegible] [illegible] alcohol with [illegible]. The insoluble [illegible] was [illegible] off and [illegible] [illegible].

The [illegible] filtrate [illegible] separation of the [illegible] [illegible] [illegible] [illegible]. The gelatinous precipitate [illegible] [illegible] [illegible] [illegible] by heating with [illegible]. The acid was identified by conversion [illegible] [illegible] [illegible].

SUMMARY

1. A method was developed for synthesis of [illegible] [illegible] double diazonium salts of antimony pentachloride.

2. A method was evolved for synthesis of [illegible] antimony compounds of the type of [illegible] and [illegible], via the double diazonium salts of antimony pentachloride.

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BROMINATION WITH DIOXANE DIBROMIDE

III. BROMINATION OF AROMATIC HYDROCARBONS AND HETEROCYCLES. A NEW METHOD OF IODINATION WITH THE HELP OF THE COMPLEX OF IODINE CHLORIDE WITH DIOXANE

A. P. Terentyev, L. I. Belenky and L. A. Yanovskaya

In the preceding papers [1, 2] we submitted the results of our work on the application of the dioxane dibromide complex to the bromination of polyhydric phenols and aliphatic aldehydes and ketones. In the present paper we report on the utilization of dioxane dibromide for bromination of aromatic hydrocarbons and some heterocyclic compounds; we also described a series of experiments with aromatic amines *.

In addition we present some results on the application of a new iodinating agent – the complex of iodine chloride with dioxane.

1. Bromination of aromatic hydrocarbons and heterocycles with dioxane dibromide

We tested the action of dioxane dibromide on benzene, toluene, naphthalene, 2-methylnaphthalene, fluorene and anthracene. It was found that benzene does not react with dioxane dibromide either at room temperature or on boiling. Toluene readily enters into reaction with dioxane dibromide on heating to 35-40° and forms p-bromotoluene in quantitative yield. Naphthalene and 2-methylnaphthalene react with dioxane dibromide even at room temperature to give the corresponding monobromo derivatives in good yield. When using a twofold excess of dioxane dibromide, naphthalene gives 1,4-dibromonaphthalene. In all cases the reaction was carried out without a solvent. Fluorene reacts in a similar way to naphthalene, forming 2-bromofluorene or 2,7-dibromofluorene depending upon the amount of reactant. The reaction of dioxane dibromide with anthracene proceeds in two ways: In presence of even the slightest trace of moisture, anthrone and anthraquinone are formed. A similar observation was earlier made by Price and Weaker [3] who brominated anthracene in dioxane with bromine. In this case the reaction undoubtedly proceeded via intermediate formation of dioxane dibromide. In absolute dioxane the bromination of anthracene proceeds at 70° and leads to 9-bromoanthracene or 9,10-dibromoanthracene depending upon the ratio of reactants.

With the objective of developing a method of bromination of acidophobic heterocyclic compounds, we tried the action of dioxane dibromide on a series of compounds of the furan and pyrrole series and also on thiphene. Furan itself in small amounts (upto5 g) is smoothly brominated by dioxane dibromide in ether or dioxane at 0° with formation of 2-bromofuran. When using large amounts of furan, however, the reaction proceeds differently, apparently with opening of the furan ring. After the reaction mixture had been worked up with water, the ether layer did not contain any other substances apart from a negligible amount of dioxane, i.e. the reaction products are water-soluble and pass into the water on washing. Treatment under anhydrous conditions (neutralization of the mixture with sodium carbonate followed by filtration) leads to separation (after removal of the ether) of a dark oil with a pungent odor which does not distil without decompositon. Sylvan is smoothly brominated by dioxane dibromide but the resultant bromosylvan is unstable and after removal of the solvent it violently and spontaneously decomposes. Judging by the outward appearance (a heavy oil with a pleasant odor) bromosylvan contains bromine in the nucleus and not in the side chain. According to the literature, 2-bromomethylsylvan is likewise unstable, but it possesses strong lachrymatory properties which were not found in our case. Furfuryl alcohol, furfural, and furfurol diacetate apparently also undergo fission by dioxane dibromide, only water-soluble products being obtained.

Pyrrole and 2,4-dimethylpyrrole are resinified on bromination with dioxane dibromide. On the other hand, 2-acetylpyrrole, 2,5-dimethyl-3-carbethoxypyrrole, 2,4-dimethyl-3-carbethoxypyrrole and 2,4-dimethyl-5-carbethoxypyrrole form the monobromo-derivatives in excellent yields. Also successfully brominated are indole to 3-bromoindole and 2-methylindole to 3-bromo-2-methylindole. 3-Methylindole enters into reaction with dioxane dibromide (decolorization of the reaction mixture), but the bromination product is unstable and decomposes in the course of

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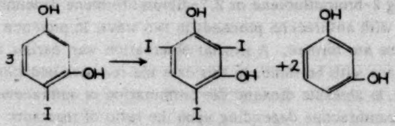
* A paper was recently published by G. M. Kosolapoff on "Direct halogenation of some aromatic amines" [J.Am. Chem. Soc., 75, 3596 (1953)]. The author mentions that complexes of dioxane with halogens can serve as mild agents for halogenation of sensitive aromatic compounds. Examples were given of the preparation of some bromo-substituted aromatic amines. The author does not cite our work on the application of dioxane dibromide although the first communication by one of us was published in 1950 (Proc. Acad. Sci. USSR, 71 693) and was abstracted in the same year in Chem. Abs., 44, 8354 (1950)(abstractor G. M. Kosolapoff).

1-2 hous after preparation. For this reason we were unable to obtain satisfactory analytical results for bromoskatole. Thiophene is brominated by dioxane dibromide to 2-bromothiophene. In all cases the bromination of heterocyclic compounds in ether or dioxane is effected at 0° or at room temperature.

Bromination of aniline or dimethylaniline under our usual conditions, i.e. in ether or dioxane solution, did not proceed smoothly: the reaction mixture turned blue and a dark precipitate appeard. The reaction proceeds differently in acetic acid. For example, on brominating dimethylaniline with dioxane dibromide in acetic acid, a good yield of p-bromodimethylaniline is obtained. Results of the reaction with aniline are also worse. With a twofold excess of dioxane dibromide, however, we succeeded in obtaining 2,4-dibromoaniline in respectable yield.

2. A new iodinating agent – the complex of dioxane with iodine chloride

None of the existing methods of iodination is really satisfactory for the iodination of acidophobic compounds. In searching for a simple and convenient method of direct iodination of acidophobic compounds, we tried out some complexes of dioxane in the iodination of active aromatic compounds (phenols) and of some accessible substances with heterocyclic structures (indole and 2-methylindole). An attempt to iodinate phenol and β-naphthol with dioxane diiodide, described by A. E. Favorsky [4], was unsuccessful. Reaction likewise failed to take place between β-naphthol and the complex of dioxane with iodine bromide [5]. Finally we employed the complex of iodine chloride with dioxane for the purpose of iodination. This substance with the composition $C_4H_8O_2$· ICl forms beautiful orange crystals [5] with m.p. 55-58°, readily soluble in organic solvents. In water and on standing in the air, dioxane-iodine chloride gradually decomposes. We did not isolate this reagent in the free state but prepared it immediately before reaction by mixing dioxane with iodine chloride. The procedure for iodination did not differ from that for bromination with dioxane dibromide. With the help of dioxane-iodine chloride, iodinations were effected of phenol, β-naphthol and salicylic acid and the monoiodo-derivatives were obtained in high yields. Iodination of resorcinol by the usual procedure leads to triiodoresorcinol, but in presence of sodium bicarbonate we succeeded in obtaining monoiodoresorcinol. Evidently under the usual conditions the initially formed monoiodoresorcinol disproportionates in presence of hydrogen chloride according to the scheme:



In the literature there is actually reported [6] a similar reaction of monoidoresorcinol dimethyl ehter under the action of a series of reagents including a solution of hydrogen chloride in ether.

In ethereal solution indole is resinified by dioxane-iodine chloride; in pyridine, however, the reaction proceeds smoothly with formation of 3-iodoindole. 2-Methylindole is also successfully iodinated to 3-iodo-2-methylindole. 3-Methylindole does not iodinate under these conditions nor under the action of iodine (when the 3-methylindole is in alkali solution [7]). N-β-Dicyanoethylindole is likewise not iodinated by dioxane-iodochloride.

EXPERIMENTAL

1. Bromination of toluene. To 9.5 g toluene was added dioxane dibromide prepared from 15.1 g bromine and a slight excess of dioxane. At room temperature the reaction does not take place to an appreciable extent. Heating (35-40°) of the reaction mixture caused rapid decolorization and separation of hydrogen bromide. The mixture was run into 10% NaOH solution and the resultant heavy oil was extracted with ether; the ethereal solution was washed with water and dried with calcium chloride. Distillation gave 16.8 g product with b. p. 182-184°; cooling with snow and salt caused the substance to solidify to easily fusible, white crystals with m.p. 26-27° (p-bromotoluene has m.p. 28.5°).

2. Bromination of naphthalene. 6.4 g naphthalene was mixed with crystalline dioxane dibromide prepared from 8g bromine. The resultant mixture quickly became liquid and then became decolorized. The reaction mixture was washed with water and extracted with ether. The ethereal layer was dried with calcium chloride and fractionally distilled. After redistillation a product was obtained (7.5g) with b.p. 148-150° (22 mm), n_D^{20} 1.6574, which agrees with the constants of 1-bromonaphthalene.

3. Bromination of 2-methylnaphthalene. 7.1 g 2-methylnaphthalene was brominated with dioxane dibromide, prepared from 8 g bromine, as described above. 8.8 g substance was isolated with b.p. 164-165° (16 mm), 139-140° (7 mm) n_D^{20} 1.6496, corresponding to 1-bromo-2-methylnaphthalene.

4. Bromination of fluorene. From 1.66 g fluorene and 2.5 g dioxane dibromide was obtained (after pouring the reaction mixture into water) 2.45 g 2-bromofluorene with m. p. 110-111° (from alcohol).

Employment of a twofold excess of dioxane dibromide and moderate heating (40-50°) of the reaction mixture to induce decolorization gave 2,7-dibromofluorene in quantitative yield with m.p. 165-166° (from alcohol).

5. Bromination of anthracene. 1.78 g anthracene was brominated in anhydrous dioxane with dioxane dibromide prepared from 0.6 ml bromine, by heating to 65-70° on a water bath. After decolorization, the mixture was poured into water and the crystals were recrystallized from alcohol; the melting point of the yellow crystals was 99-99.5°, corresponding to 9-bromoanthracene. The yield of the recrystallized product was quantitative.

Employment of a twofold excess of dioxane dibromide under the same conditions gave a quantitative yield of 9, 10-dibromoanthracene with m.p. 224-225° (from xylene).

6. Bromination of furan. 4.2 g furan was brominated in dioxane solution, while cooling with snow, by gradual addition of a solution of 16 g dioxane dibromide in dioxane. The resultant transparent solution was poured into a solution of sodium carbonate and the oil which separated was steam-distilled. The distillate was extracted with ether. The ethereal extract was dried with anydrous magnesium sulfate and carefully fractionated. Yield 7 g 2-bromofuran with b.p. 103-104° and n_D^{20} 1.4980, in agreement with the literature data.

7. Bromination of sylvan. 16.4 g sylvan was brominated with 50 g dioxane dibromide in ether-dioxane solution at 0°. The solution was thoroughly washed with water, alkali and again with water, and dried with anydrous magnesium sulfate; the ether was cautiously distilled off. The residue contained a heavy oil with a pleasant odor which in 15-20 minutes suddenly and violently decomposed with evolution of hydrogen bromide and formation of a black resin. All attempts to isolate the oil in the pure state, apply steam distillation, were unsuccessful; on heating, the oil instantaneously decomposed.

8. Bromination of indole. 0.59 g indole was brominated in ether solution at 0° by addition in small portions of a solution of dioxane dibromide (from 0.256 ml bromine) in ether. The reaction mixture was washed with sodium bicarbonate solution, and with water and dried with anydrous sodium sulfate. After evaporation of the ether, a residue of silver white leaflets of 3-bromoindole was obtained; m.p. 67° (with decomp.) from ligroine. The leaflets quickly darkened when kept. Yield 0.59 g (60% of the original indole).

9. Bromination of 2-methylindole. 1.31 g 2-methylindole was brominated with 2.5 g dioxane dibromide in a similar manner to indole to give 1.68 g 3-bromo-2-methylindole with m.p. 86-87° (from ligroine); a mixed test with a sample of 3-bromo-2-methylindole prepared by bromination of 2-methylindole with chloramine T and potassium bromide [8] did not give a depression.

10. Bromination of 3-methylindole. 0.65 g 3-methylindole was brominated with 1.25 g dioxane dibromide in the same manner as indole. Evaporation of the ether from the dried ethereal layer left 0.70 g crystalline product with m.p. 77° (with decomp. from ligroine). After keeping for a short period (1-2 hours), however, the product darkened and decomposed. We were consequently unable to obtain precise analytical data: the C, H and Br contents of the product varied sharply in the course of analyses of a single sample. From the results of the first determination the bromine content is about 40%; the composition is close to that of a monobromo- derivative (bromine content 38.6%).

11. Bromination of 2,5-dimethyl-3-carbethoxpyrrole. To 1.67 g 2,5-dimethyl-3-carbethoxypyrrole in 15 ml dioxane was introduced little by little 2.5 g dioxane dibromide at room temperature. The color changed to brownish-violet. The reaction mixture was poured into water, and the precipitate was collected, washed with water and recrystallized from aqueous alcohol. Yield 2.4 g with m.p. 130° (on rapid heating); on slow heating the product decomposes and blackens at 104°.

4.110 mg sub.: 6.625 mg CO_2; 1.850 mg H_2O; 1.335 mg Br. 5.400 mg sub.; 8.710 mg CO_2; 2.450 mg H_2O; 1.755 mg Br. Found %: C 43.99, 44.03; H 5.04, 5.08; Br 32.48, 32.50. $C_9H_{12}O_2NBr$. Calculated %: C 44.10 H 4.94 Br 32.61.

2,5-Dimethyl-3-carbethoxy-4-brompyrrole was here prepared for the first time.

12. Bromination of 2-acetylpyrrole. 3.6 g 2-acetylpyrrole was brominated in 30 ml dioxane at room temperature with 9.5 g dioxane dibromide. The mixture was poured into water and the precipitate filtered and dried to give 3.5 g bromo-2-acetylpyrrole with m.p. 108° (with decomp.).

9.025 mg sub.: 0.552 ml N_2 (21°, 761 mm). 5.465 mg sub.: 0.340 ml N_2 (21°, 761 mm). Found %: N 7.11, 7.23. C_6H_6ONBr. Calculated %: N 7.45. 5.575 mg sub.: 7.853 mg CO_2; 1.580 mg H_2O; 2.404 mg Br. 4.270 mg sub.:

6.027 mg CO_2; 1.290 mg H_2O; 1.825 mg Br. Found %: C 38.44, 38.52 H 3.17, 3.30; Br 43.01, 42.72. C_6H_6ONBr. Calculated %: C 38.33; H 3.22; Br. 42.51.

We did not establish the structure of bromo-2-acetylpyrrole.

13. Bromination of 2,4-dimethyl-3-carbethoxypyrrole. Bromination with 2.5 g dioxane dibromide in dioxane at room temperature gave 5-bromo-2,4-dimethyl-3-carbethoxy pyrrole. Yield 95%. m.p. 96° (from alcohol).

14. Bromination of 2,4-dimethyl-5-carbethoxypyrrole. Procedure as before. A quantitative yield of 3-bromo-2,4-dimethyl-5-carbethoxypyrrole was obtained; m.p. 150-151° (from alcohol).

15. Bromination of thiophene. 3.36 g thiophene was brominated in ether solution with 7.5 g dioxane dibromide while stirring and cooling with water; after working up as usual, fractionation gave 6.5 g 2-bromothiophene with b.p. 43-44° (15 mm), n_D^{20} 1.5868.

16. Bromination of acetanilide. To a solution of 1.35 g acetanilide in dioxane was added 2.5 g dioxane dibromide. The mixture quickly decolorized. After pouring into water, 2.1 g p-bromoacetanilide was obtained with m.p. 167-168° (from alcohol).

17. Bromination of N,N-dimethylaniline. To a solution of 12.1 g N,N-dimethylaniline in acetic acid was added 25 g dioxane dibromide in 1-2 g portions with shaking; the solution quickly decolorized. The mixture was run into a large volume of dilute alkali and an oil separated out which soon crystallized after treatment with water. Yield 2 g 4-bromo-N,N-dimethylaniline. m.p. 55-56° (from aqueous alcohol).

18. Bromination of aniline. To a solution of 9.3 aniline in acetic acid was added 50 g dioxane dibromide in the manner described above. The darkened solution was run into dilute alkali. The precipitate was collected, washed with water and recrystallized from aqueous alcohol. Yield 14.5 g product with m.p. 79-80° (2,4-dibromoaniline).

19. Iodination of phenol. To a solution of 3 g phenol in 30 ml carbon tetrachloride was gradually added a mixture of 4.9 g iodine chloride and 5 ml dioxane. After 1 1/2 hours the mixture was washed with sodium carbonate solution and dried with fused potassium carbonate. The oil remaining after evaporation of the solvent crystallized on rubbing in presence of water. Yield 5.1 g monoiodophenol (mixture of o- and p-isomers). Pure p-iodophenol with m.p. 93° was isolated by fractional precipitation with carbon dioxide gas from a solution of the iodophenol in 10% NaOH.

20. Iodination of salicylic acid. To a solution of 1.8 g salicylic acid in 5 ml dioxane was added with stirring a solution of 2.1 g iodine chloride in 3 ml dioxane. The next day the mixture was poured into sodium sulfate and 3 g 5-iodosalicylic acid was obtained with m.p. 192° (from aqueous alcohol).

21. Iodination of β-naphthol. To a solution of 1.4 g β-naphthol in 5 ml ether was added a mixture of 1.5 g iodine chloride and 2 ml dioxane. Working up in the usual way gave 2.4 g 1-iodo-2-naphthol with m.p. 94.5° (from dilute alcohol).

22. Iodination of resorcinol. To 1.65 g resorcinol in 20 ml ether was added a solution of 2.4 g iodine chloride in 5 ml dioxane and 10 ml ether. Working up was carried out as usual after 1 hour. Evaporation of the ether left a poorly crystallizing oil which crystallized after treatment with water and standing. Yield 1.2 g 2,4,6-triiodoresorcinol with m.p. 144°.

1.3 g resorcinol was iodinated in 20 ml ether in presence of 2 g sodium bicarbonate powder with a mixture of 1.5 g iodine chloride and 5 ml dioxane. The usual treatment followed by evaporation of the ether gave 2.15 g oil which slowly (in the course of several weeks) crystallized. The crystals had m.p. 60°; after standing in the air the melting point rose to 93°. Due to the high solubility of the substance in water and organic solvents, it could not be recrystallized. According to the literature, 4-iodoresorcinol crystallizes with one molecule of water and the monohydrate has m.p. 63°; on standing in the air the water is lost; the melting point of the anhydrous preparation is 100° [9].

23. Iodionation of indole. To a solution of 0.6 g indole in 5 ml pyridine was added, with stirring and snow cooling, a mixture of 0.85 g iodine chloride and 5 ml dioxane. The resultant solution was poured into water and extracted with ether. Evaporation of the ether left 1.2 g 3-iodoindole with m.p. 75° (with decomp.; from ligroine).

24. Iodination of 2-methylindole. 0.5 g 2-methylindole was iodinated with a mixture of 0.65 g iodine chloride and 5 ml dioxane under the conditions of iodination of indole. Yield 0.65 g 3-iodo-2-methylindole with m.p. 81.5° (from ligroine).

SUMMARY

1. Dioxane dibromide is a mild brominating agent for a series of aromatic hydrocarbons and amines, thiophene, and some derivatives of pyrrole and indole.

2. A new method of iodination is proposed with the help of the dioxane-iodine chloride complex and is applied to phenols and some indoles.

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SUMMARY

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2. A new method of iodination is proposed with the dioxane-iodine chloride complex and is applied to phenol and some indoles.

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THE STRUCTURE OF PALUSTROL

N. P. Kiryalov

Palustrol, a saturated tertiary tricyclic alcohol of the composition $C_{15}H_{26}O$ was first[1] isolated from the essential oil of the marsh rosemary (Ledium palustre L.).

Not long ago investigations [1, 2] showed that palustrol belongs to the group of azulene-forming sesquiterpene alcohols since on heating with dehydrogenating agents (S, Se, Pd) palustrol readily forms a blue liquid containing 1,4-dimethyl-7-isopropylazulene (picrate with m.p. 121-122°).

It is also important to note that on heating with acids (H_2SO_4, HCl, HCOOH) palustrol is dehydrated with facility to form bicyclic or tricyclic hydrocarbons with the formula $C_{15}H_{24}$, which justifies the assumption that palustrol belongs to the group of tertiary tricyclic alcohols. As the investigations showed [1, 2], under mild dehydration conditions palustrol splits off water with formation of tricyclic hydrocarbons containing one double bond, while under more drastic conditions dehydration leads to more far-reaching modification involving scission of the cyclopropane ring (the presence of a cyclopropane ring was demonstrated by physical methods and by the reactions of the compound) and formation of bicyclic hydrocarbons with two double bonds.

On comparing the above-mentioned results of investigation of palustrol with what is known about the chemical properties of ledol [3, 4], we see that palustrol and ledol are almost identical in their behavior toward acids or dehydrogenating agents and that they form very similar or identical products of reaction. These facts suggest a similarity of structure of both these compounds, although palustrol and ledol possess different physical properties (Table 1).

TABLE 1

Compound	Formula	Boiling point	α^{20}_D	Melting point	Odor
Palustrol	$C_{15}H_{26}O$	276-278°	−17°	Liquid	Musty odor
Ledol	$C_{15}H_{26}O$	282-283°	+5°	105-106.5°	Nearly odorless

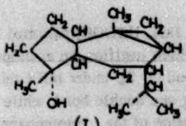
The results of a further study of palustrol described in the present paper confirm the similarity between the structures of palustrol and ledol. This facilitates the elucidation of the structure of palustrol since that of ledol is already known [4] and corresponds to structural formula (I).

Palustrol was isolated from marsh rosemary oil and dehydrated, and the resultant tricyclic hydrocarbons, palustrenes [probable structures (III) and (IV)], were oxidized. Oxidation gave two crystalline substances – ledic acid $C_{15}H_{24}O_3$ [m.p. 155-156°; probable structure (V)] and ledglycol $C_{15}H_{26}O_2$ [m.p. 151-152°; probable structure (VI)]. These derivatives were previously found, as reported [3, 4], among the products of oxidation of ledene. The yield of ledglycol and ledic acid on oxidation of the mixture of palustrenes, however, differs considerably from the yield of these compounds after oxidation of the mixture of ledenes. Thus the oxidation of a mixture of ledenes gave 40-50% ledglycol and 1-2% ledic acid, whereas oxidation of the mixture of palustrenes gave only 20-30% ledglycol (or in the most favorable case 25%) and 7-10% ledic acid. It should be observed that the low yield of ledglycol on oxidation of palustrenes may be explained to a certain extent by the fact that 15-20% of the ledglycol could not be crystallized from the products of oxidation. The presence of ledglycol in the mother liquor of the oxidation products could be inferred from our isolation from the mother liquor of an unsaturated ketone – $\Delta^{5,6}$-2,5-dimethyl-8-isopropyl-1-octalone (VIII) – the product of dehydration of ledglycol in an acidic medium which is accompanied by rearrangement [4].

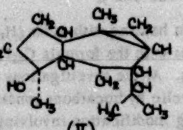
Originally we suggested that specimens of palustrol at our disposal and used for the investigation (Table 2) contain a considerable amount of ledol as impurity (of the order of, say, 50%), since only a very high content of ledol in palustrol could entitle us to say that the results of oxidation of palustrenes were not determined by the structure of palustrol. To verify this hypothesis, various samples of palustrol (Table 2) were subjected to cooling (to −60°) and to fractional distillation. Neither method gave indication of the presence of considerable amounts of ledol in the investigated samples of palustrol. The presence of traces or even small amounts (up to 1-2%) ledol in the sample of palustrol is certainly possible. The separation of the impurities by physical methods, however, was extremely difficult and was not of material importance for the present investigation. It was important to establish that the main products of oxidation of palustrenes (from palustrol) were identical with the products of oxidation of ledenes (from ledol).

Bearing in mind that dehydration of palustrol was performed under conditions similar to those of dehydration of ledol and that no double bond translocations were observed on distillation of palustrenes (palustrenes form identical crystalline products before and after distillation, i. e. ledic acid and ledglycol), it is reasonable to assume that the hydroxyl group of ledol and palustrol is attached to the same carbon atom. Palustrol consequently differs from ledol in that palustrol is either a levorotatory optical isomer of ledol or a levorotatory diastereomer of ledol. We hold to the view that palustrol is a levorotatory diastereomer of ledol because the rotatory power of ledol is $[\alpha]_D$ +5°; α_D + 5° (c = 10; in alcohol), whereas palustrol has $\alpha_D - 17°$ (± 0.4°).

On the assumption that ledol has structure (I), we may suggest structure (II) for palustrol; this differs from (I) only in the spatial position of the hydroxyl group.

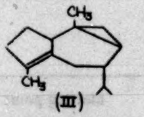


(I)

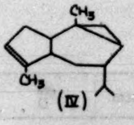


(II)

On the basis of structure (II) we may suggest that dehydration of palustrol gives mainly α- and β-palustrenes [probable structures (III) and (IV)]; γ-palustrene [possible structure (VII)] is not formed. Oxidation of β-palustrene gives ledic acid (V), while α-palustrene gives ledglycol (VI).



(III)



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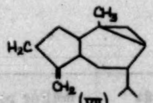

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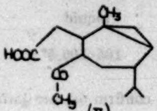

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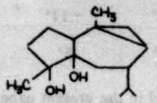

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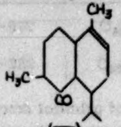

(VIII)

The possibility of formation of hydrocarbons (III) and (IV), and also of compounds (V) and (VI) has already been indicated [3, 4].

On the basis of a comparison of the structural formulas of α- and β-palustrenes with those of α- and β-ledenes [4] we may conclude that they are identical and that the names of the hydrocarbons are synonymous. This conclusion is obviously correct because ledglycol and ledic acid prepared by oxidation of ledenes or palustrenes possess the same sign and magnitude of rotation.

TABLE 2

Properties of the palustrol used in the investigation

Specimen number	d_{20}^{20}	n_D^{20}	α_D	Boiling point	Percent alcohol by the Chugaev-Zerewitinov method
1	0.9593	1.4911	−16.9°(18°)	123-126° (2 mm)	99.4
2	0.9615	1.4914	−16.5 (18°)	128-131 (3 mm)	99.6
3	0.9588	1.4917	−16.65 (21°)	127-131 (2-3 mm)	96.87
4	0.9643	1.4916	−17.1 (25.5°)	130-132 (3 mm)	101.2
5	0.9593	1.4908	−17.35 (20°)	127-131 (3 mm)	99.0

EXPERIMENTAL

Specimens of palustrol (Table 2) were obtained from marsh rosemary oil by the previously described procedure [2].

Palustrol was additionally characterized by the determination of its Raman spectrum. A ISP-51 spectrograph was used; the light source was a quartz-mercury lamp (excited by the λ 4358.3 A line); width of slit 0.007 mm; period of exposure 3 hours.

The Raman spectrum of palustrol contains the following lines ($\Delta\nu$ in cm^{-1}): 261 (5), 295 (1), 332 (2), 444 (10), 475 (2), 508 (2), 636 (1), 706 (10), 757 (5), 790 (10), 827 (2), 870 (4), 977 (10), 1094 (1), 1242 (5), 1304 (1), 1342 (1), 1441-1454 (10). *

Behavior of palustrol at low temperatures

1. On cooling to −60° palustrol is transformed into a vitreous mass which becomes liquid at −40°.

2. An alcohol solution (1:3) of palustrol changes into a slurry at −55° but again forms a transparent solution at −43°. Ledol does not separate on rapid filtration at the pump at low temperatures. Introduction into a cooled solution of palustrol of a small crystal of ledol does not cause crystallization and the crystal remains undissolved.

3. 1 g ledol and 2 g palustrol were dissolved in 5 ml 80% ethyl alcohol and the solution was cooled to −15°; the ledol (1 g) separated unchanged.

Dehydration of palustrol

40 g palustrol was dissolved in 80 ml 96% alcohol and run into a solution of 4 ml sulfuric acid in 8 ml alcohol. The mixture was heated to the boil; when the liquid had become cloudy, gentle heating was maintained for eight minutes. The upper oily layer (40 ml) was separated, washed with water, dried with sodium sulfate and distilled at 5-6 mm over Na. Two fractions were obtained: 1st– b.p. up to 130°, 29 g; 2nd – b.p. 130-135°, 5.3 g. The first fraction was redistilled over Na to give a colorless oil with b.p. 112-115° (5 mm). Yield about 25 g.

n_D^{18} 1.4978, d_{20}^{20} 0.9207

Found %: C 88.06; H 11.72. $C_{15}H_{24}$. Calculated %: C 88.16; H 11.84.

In properties the oil closely resembles the hydrocarbon palustrene [2].

Dehydrogenation of palustrene

3 g palustrene and 2 g selenium were heated to 240-255° for 3 hours. The mixture quickly became violet. The oil was distilled with steam and dissolved in low-boiling gasoline and the azulene was extracted with 90% phosphoric acid. The phosphoric acid extract was diluted with water and the separated oil was extracted with ethyl ether. The ethereal solution was dried with sodium sulfate and the ether distilled off. The residue was a violet oil, weight about 0.2 g. To this oil was added a saturated alcoholic solution of picric acid (0.2 g). A picrate was obtained in the form of dark needles with m.p. 121-122° (after three recrystallizations from alcohol). The picrate did not give a depression in a mixed test with the picrate of 1,4-dimethyl-7-isopropylazulene. The picrate of the product of dehydrogenation of ledene is known to have m.p. 122-123° and does not differ from the picrate of 1,4-dimethyl-isopropylazulene [4]. The previously prepared [2] picrate with m.p. 118-119° was evidently insufficiently pure.

Oxidation of palustrene

20 g palustrene was dissolved in 700 ml acetone and to the solution was gradually added a solution of potassium permanganate (30 g $KMnO_4$ in 300 ml water). After decolorization of the solution, the manganese dioxide was filtered off and washed with acetone and hot water. The acetone was distilled off, the supernatant oily layer was collected and the aqueous layer was extracted with ether. Acidification of the aqueous solution gave a voluminous precipitate. M.p. 155-156° (from aqueous alcohol); $[\alpha]_D^{20}$ + 127°. The substance did not give a depression in a mixed melting test with ledic acid of the composition $C_{15}H_{24}O_3$, prepared by oxidation of ledene [3]. Yield 1.4-2 g (i.e. up to 10% of the original hydrocarbon).

Found %: C 71.44; H 9.55. $C_{15}H_{24}O_3$. Calculated %: C 71.39; H 9.58.

The ethereal solution was dried with sodium sulfate and the ether was distilded off to leave a partly crystallizing oil. The crystalline portion had m.p. 151-152° (from gasoline); $[\alpha]_D$ −18.2° (c = 5; in alcohol). The product did not give a depression of melting point in admixture with a pure preparation of ledglycol [3]. Yield 4g (approx. 20%).

Found %: C 75.52; H 11.08. $C_{15}H_{28}O_2$. Calculated %: C 75.58; H 10.99.

In addition to ledic acid and ledglycol, 14.85 g liquid products of oxidation was obtained. From the liquid portion 4 ml volatiles was distilled off with steam. Into the residue of non-steam-distillable oxidation products was run

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* The figures in brackets refer to the intensities of the lines as visually evaluated.

sulfuric acid in such quantity that the solution had 2% concentration; the steam distillation was then resumed. About 4 ml dark-red liquid was collected. B.p. 130-145° (3 mm), n_D^{24} 1.5080, d_{20}^{20} 0.9742. The liquid was crude $\Delta^{5,6}$-2,5-dimethyl-8-isopropyl-1-octalone (VIII), as was confirmed by the following two reactions.

1. 1 g substance in admixture with 1 g selenium was heated to the boil (260-280°) for 4 hours. A substance was obtained with $n_D^{18.5}$ 1.532 and forming a picrate with m.p. 130-131° (from alcohol). The picrate did not give a depression in a mixed melting test with the picrate of the unsaturated 2,5-dimethyl-8-isopropyl-1-tetralone [4].

2. Oxidation of 3 g of the oil, dissolved in 150 ml acetone, with potassium permanganate (3 g $KMnO_4$ in 50 ml water) gave 2.5 g neutral (partially crystallizing) products of oxidation containing about 0,6 g pure substance with m.p. 180-182° (from gasoline). This substance did not give a depression in a mixed melting test with the known ketoglycol with the formula $C_{15}H_{26}O_3$ (m.p. 183-185°) previously prepared by oxidation of $\Delta^{5,6}$-2,5-dimethyl-8-isopropyl-1-octalone.

SUMMARY

Evidence is adduced to show that palustrol is the levorotatory diastereomer of ledol.

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* T.p. = C.B. Translation pagination.

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HIGHER BARIUM PHOSPHIDES

S. A. Shchukarev, M. P. Morozova, and E. A. Prokofyeva

It was recently shown [1] that in the system barium-nitrogen, together with ordinary barium nitride Ba_3N_2, it is possible to obtain, in a state of thermodynamic equilibrium with their decomposition products, the higher nitrogen compounds. The existence of these higher barium nitrides could have been predicted on the basis of their heats of formation, determined with the aid of the isoatom method [2], for which reason their synthesis was undertaken.

With the aid of this isoatom method it is possible to show that in a series of analogous binary systems (systems, composed of a single element on the one hand, and of the elements of a single subgroup of the periodic system on the other hand) the forms of the thermodynamically stable compounds shift in the direction of enriching the components for which the atomization enthalpy* is lower. The higher barium nitrides are formed under conditions of high nitrogen pressure. Inasmuch as the atomization enthalpy of phosphorus (31.6 kcal) is considerably less than the atomization enthalpy of nitrogen (85 kcal), it may be assumed that the higher barium phosphides (BaP_2, BaP_3) can be obtained in a state of thermodynamic equilibrium at low pressures of phosphorus vapors.

Actually, it was found that the reaction of metallic barium with phosphorus vapors at a temperature of 400-450°, with subsequent removal of excess phosphorus by vacuum distillation at the same temperature, leads to the formation of a dark gray product having the composition BaP_3.

The chemical analysis method, carried out in the following manner, was used to establish the formula of this compound.

The substance was transferred to a tared ampoule in an atmosphere of dry carbon dioxide gas, after which the ampoule was sealed and weighed. The sealed ampoule containing the analyzed substance was placed in a vessel, from which the air was removed by evacuation. On reaching a vaccum of the order of 10^{-2} mm the evacuation was terminated, the ampoule was broken, and concentrated nitric acid was added dropwise and with extreme care to the vessel, the purpose of the nitric acid being to oxidize the phosphorus hydrides to orthophosphoric acid.

The subsequent determination of the amount of barium and of phosphous was performed in the usual manner.

Found %:** Ba 59.95; P 39.90. BaP_3. Calculated %: Ba 59.65; P 40.35.

The heating of the compound having this composition in vacuum at a temperature of 740-840° leads to the partial removal of phosphorus and the formation of a product, the composition of which approximates BaP_2. Data on the composition of the preparations obtained in our experiments are given in the table.

TABLE

Ba (in %)	P (in %)	Atomic ratio
68.4	30.6	1:1.984
68.6	30.8	1:2.002
69.1	30.8	1:1.976
68.4	30.4	1:1.970

It should be mentioned that even extremely prolonged (up to 20 hours) heating of this preparation in vacuum at a temperature of 780-840° fails to lead to further removal of phosphorus and the formation of the ordinary phosphide having composition Ba_3P_2. As a result, it can be assumed that the decrease in the atomization enthalpy on going from nitrogen to phosphorus makes the form, Ba_3P_2, corresponding to the normal valencies of barium and phosphorus, thermodynamically unfavorable.

The X-ray pattern of the preparation having a composition corresponding to the formula BaP_2, contains all of the lines found in the X-ray pattern for BaP_3 and, in addition, contains a series of new lines. The preparations were obtained at different temperatures; consequently, despite the excellent agreement of the results of numerous analyses, it is still difficult for us to draw any final conclusions as to wherher BaP_3 is an individual substance.

The final decision as to the number of phases in the system barium-phosphorus can be made on the basis of tensimetric measurements. As yet, only the existence of the compound BaP_2 can be considered as being established.

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* We designate as the atomization enthalpy the enthalpy of transforming the element from its standard state into the state of a single atomic pair, referred to one gram-atom.

** Average of 6 determinations.

In due time some consideration was given [3] to the phenomenon of secondary periodicity, a discovery made by Byron in 1915. It was also shown that the phenomenon of secondary periodicity is very clearly manifested in the enthalpy values for the formation of binary compounds from the elements of the major subgroups, especially in the case of those compounds in which the elements show a valency corresponding to the number of the group.

An increase in the enthalpy of formation is observed on transition from an element of the second series to one of the third, a decrease is observed when the transition is from the third to the fifth series, then an increase is observed when the transition is from the fifth to the seventh series, and, finally, a decrease is again observed on transition to the ninth series. Together with the secondary periodicity of the heats of formation, as is shown by our data, there also exists a secondary periodicity of the higher forms of thermodynamically stable compounds.

The higher thermodynamically stable compound of barium with nitrogen is BaN_2, with phosphorus it is apparently BaP_3. In any case, the stability of BaP_2, i.e., the compound that is analogous to the higher form of barium nitride (BaN_2), is considerably greater than the nitride.

As was shown in some preliminary experiments, the reaction of barium with arsenic failed to give any compounds that were very rich in the nonmetallic element.

SUMMARY

1. The esixtence of the compound BaP_2 in the system barium-phosphorus was established. Also, the existence of BaP_3 was not excluded.

2. In accord with the prediction, based on the isoatom method, it was experimentally established that there is an increase in bond strength when going from nitrogen to phosphorus.

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SOLUTION REACTIONS BETWEEN ZIRCONIUM NITRATE AND ALKALI METAL IODATES

II. THE COMPOSITION OF ZIRCONIUM IODATE PRECIPITATES WHEN ALLOWED TO STAND WITH SOLUTIONS CONTAINING POTASSIUM IODATE

M. I. Konarev and A. S. Solovkin

It was shown earlier [1] that hydroxyiodates are present in the precipitate that is obtained when potassium iodate is added to zirconium nitrate solutions. Precipitates having the two compositions given below were isolated:

1) $Zr(OH)_3IO_3 \cdot 4H_2O$ and 2) $ZrOH(IO_3)_3 \cdot 4H_2O$.

The monoiodate is precipitated from aqueous zirconium nitrate solutions with either small or large amounts of added potassium iodate. From nitric acid solutions zirconium monoiodate is precipitated only when small amounts of potassium iodate are added. When a large excess of potassium iodate is added to the solution the only product found in the precipitate is zirconium triiodate.

Both the monoiodate and the triiodate precipitates, being amorphous, on long standing with the mother liquors containing potassium iodate, are converted into fine crystals.

With the objective of establishing the relationship existing between the structure of the precipitate and its composition, we studied: 1) the change in the composition of the precipitates with time, and 2) the compositions of the crystalline precipitates.

EXPERIMENTAL

Crystallization rate of zirconium iodate precipitates. On allowing zirconium monoiodate to stand with the mother liquor, containing potassium iodate, the precipitate begins to crystallize but the process takes place very slowly. After allowing to stand for 1.5 months we are unable to obtain complete crystallization of the precipitates. When zirconium triiodate is allowed to stand with the mother liquors the crystallization of the precipitates proceeds much more rapidly, which process is favored by the presence of nitric acid in the solution, the function of the nitric acid being to prevent hydrolysis (Table 1).

The values given in Table 1 show that the reaction is not terminated with the formation of zirconium triiodate. On changing the structure of the precipitate the composition also undergoes a change. On standing with the mother liquor, the initially precipitated triiodate adds potassium and iodate groups, hydroxyl groups and water being removed from the compound (Experiment Nos. 3-6, 11, 12, 17 and 19).

The reaction of the triiodate precipitate with potassium iodate contained in the solution takes from several hours to many days, depending on the concentration of potassium iodate and the acidity of the solution. With increase in the solution concentration of potassium iodate, and also on lowering the acidity, the rate of change in composition increases, and the crystallization rate is accelerated. Only at extremely low acid concentrations (pH 2-3), due to hydrolysis of the precipitates (formation of $Zr(OH)_3IO_3 \cdot 4H_2O$) is their rate of reaction with potassium iodate markedly retarded.

The crystalline precipitates, in contrast to the amorphous precipitates, do not contain any water of crystallization. The compounds that are formed are less soluble than zirconium triiodate.

Composition of the crystalline zirconium iodate precipitates. The experiments were carried out with nitric acid and water solutions of zirconium nitrate. When working with nitric acid solutions the precipitant used was potassium iodate, dissolved in nitric acid, which also served to dissolve the zirconium nitrate. When working with water solutions of zirconium nitrate the precipitants used were mixtures of iodic acid with potassium iodate. In the starting nitrate solutions the amount of zirconium was about 1.4 g/liter. The precipitant was added in a volume equal to the volume of the zirconium nitrate solution.

TABLE 1

Change in the Composition of Zirconium Iodate with Time

Exp No.	Time	Found in mother liquor (in g/liter)		Found in precipitate (in %)						Ratio in the precipitate K : Zr : IO_3 : H_2O	Character of the precipitate
		IO_3	Zr	K	Zr	IO_3	NO_3	H_2O	Total		
						1.4 N HNO_3					
1	10 min.	15.9	11.0	None	12.59	73.16	0.04	9.91	96.7	0 : 1 : 3.03 : 4.0	Amorphous
2	3 hours	15.9	9.9		12.89	73.37	0.14	10.12	96.4	0 : 1 : 2.97 : 4.0	Amorphous
3	24 hours	15.5	9.6	6.14	8.82	84.67	0.02	2.90	96.7	1.62 : 1 : 5.01 : 1.6	Mixture of amorphous with crystalline
4	32 hours	15.1	7.0	6.70	6.55	87.01	–	0.15	99.5	2.39 : 1 : 6.93 : 0	Crystalline
5	72 hours	14.6	4.9	6.65	6.75	87.23	–	0.00	99.0	2.30 : 1 : 6.74 : 0	
6	120 hours	14.7	5.1	6.64	6.77	87.32	–	0.04	99.2	2.29 : 1 : 6.73 : 0	
						5.5 N HNO_3					
7	10 min.	32.2	15.8	None	12.52	75.12	0.12	10.10	97.7	0 : 1 : 3.13 : 4.1	Amorphous
8	8 hours	32.1	14.5		13.26	73.06	0.06	10.03	96.7	0 : 1 : 2.86 : 3.9	
9	24 hours	32.2	14.5		13.13	72.53	–	9.71	95.3	0 : 1 : 2.88 : 3.8	
10	33 hours	32.2	14.2		13.24	74.23	–	–	–	0 : 1 : 2.92	
11	168 hours	31.2	10.0	5.43	8.10	84.22	–	–	97.8	1.56 : 1 : 5.42	Greater part crystalline
12	240 hours	30.9	6.4	6.16	7.44	85.70	–	–	99.3	1.93 : 1 : 6.00	Crystalline
						5.7 N HNO_3					
13	10 min.	69.2	13.3	None	11.85	74.80	0.04	–	–	0 : 1 : 3.29	Amorphous
14	1 hour	69.0	11.1		13.01	74.44	0.14	–	–	0 : 1 : 2.99	
15	2 hours	68.7	10.4	0.7	13.00	74.49	–	–	–	0 : 1 : 2.99	
16	5 hours	66.7	9.6	–	7.08	83.59	–	–	–	–	
17	8 hours	66.4	7.4	6.24	7.14	85.40	–	–	–	2 04 : 1 : 6.24	Crystalline
18	12 hours	65.9	7.8	–	7.20	84.80	–	–	–	–	
19	60 hours	65.5	5.9	6.03	7.13	85.11	–	–	–	1.97 : 1 : 6.23	

In studying the variation in the composition of the precipitate as a function of the potassium iodate concentration and of the acidity of the solution, it was found necessary to make a large number of experiments. The obtained results are divided into two groups and are given in Tables 2 and 3.

The composition of each separately analyzed precipitate is not given in Table 2. In the table are given the potassium iodate concentration intervals, within which limits precipitates are obtained with varying amounts of iodate groups per 1 atom of zirconium. In Table 3 are given the results obtained on analyzing the precipitates with whole number ratios between the iodate groups and potassium.

The data given in Table 2 show that on increasing the concentration of potassium iodate, with the acidity of the solution kept constant, the amount of iodate groups and of potassium is increased with respect to the amount of zirconium found in the precipitate.

The formation of compounds with whole number relationships between the components is not characteristic for the crystalline zirconium iodates, for which reason sharp transitions in the compositions are not observed. Only by the method of judicious selection of the amount of excess potassium iodate (at the given acidity of the solution) is it possible to obtain precipitates with whole number relationships between the iodate groups and zirconium (6 : 1, 7 : 1, 8 : 1 and 9 : 1). At potassium iodate concentrations lower than that needed for the formation of the iodate with six iodate groups per 1 atom of zirconium, a portion of the precipitates remains amorphous.

The composition of the crystalline zirconium iodates is determined not only by the concentration of potassium iodate, but also by the acidity of the solution. With increase in the acidity the addition of iodate groups, and especially of potassium, is made difficult; consequently in order to obtain precipitates of the same composition in more highly acidic solutions it is necessary to use a higher concentration of potassium iodate. When a mixture of iodic acid and potassium iodate is used as the precipitant, both the total concentration of iodate ions in solution and the ratio between iodic acid and potassium iodate possess considerable significance.

TABLE 2

Change in the Composition of Zirconium Iodate Precipitates with Change in the Acidity and Concentration of Potassium Iodate in the Solution

Concentration of acid in the solution	Amount of IO_3-groups in the precipitate per 1 atom of zirconium						Number of iodate groups found per 1 atom of potassium	Number of investigated precipitates
	from 6 to 7	from 7 to 8	from 8 to 9	from 6 to 7	from 7 to 8	from 8 to 9		
	IO_3 concentration in the solution (in moles/liter)			Number of K atoms found per 1 atom of zirconium				
			Nitric acid solutions					
0.18	0.070-0.095	0.095-0.150	Not formed on saturating the solution with KIO_3	2.0-2.3	2.3-2.6	–	~ 3	9
0.48	0.080-0.120	0.120-0.240						15
0.98	0.085-0.130	0.130-0.270						16
1.75	0.100-0.140	0.140-0.310						14
3.3	0.135-0.190	0.190-0.300	0.300-0.400*	1.6-2.0	2.0-2.6	2.6-2.8	~ 3	12
4.2	0.150-0.250	0.250-0.320	Not formed					8
			Iodic acid solutions					
0.062	Not determined	0.140-0.310	0.310-0.358	2.0-2.35	2.35-2.65	3	~ 3	5
0.084	0.100-0.140	0.140-0.290	0.290-0.350					13
0.166	Not determined	0.275	0.235-0.284					3
0.248	0.270	0.378-0.390	0.280-0.305					10

TABLE 3

Composition of the Precipitates with Integer Amounts of Iodate Groups

Number of iodate groups found per 1 atom of zirconium in the precipitate	Amount in the precipitate (in %)				Ratio in the precipitate		Number of investigated precipitates
	K	Zr	IO_3	Total	K : Zr	IO_3 : K	
3	None	12.92	75.17	88.09	–	–	8
6	6.40	7.33	85.35	99.1	2.04	3.00	6
7	6.19	6.36	86.41	99.0	2.25	3.16	4
8	6.24	5.69	87.45	99.4	2.60	3.09	8
9	6.49	5.18	88.95	100.6	2.93	3.06	3

In the experiments with the nitric acid solutions we were able to obtain precipitates containing only up to 8.6 iodate groups per 1 atom of zirconium. In the experiments where mixtures of iodic acid and potassium iodate served as the precipitants, we were able to obtain precipitates containing up to 9 iodate groups per 1 atom of zirconium.

Two atoms of potassium are present in the precipitate containing 6 iodate groups per 1 atom of zirconium. Further increase in the number is more rapid for the iodate groups than it is for potassium. The following rule holds true for expressing the relationship that exists between increase in the number of iodate groups and the increase in potassium: in all crystalline precipitates, in which number are also included those precipitates having fractional ratios between the iodate groups and zirconium, the ratio of the iodate groups to potassium is expressed by a constant, equal to 3.

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* The mole ratio of IO_3 to zirconium was 8.6 : 1.

The constancy of the ratio values between the iodate groups and potassium (with fractional ratios between the iodate groups and zirconium, also between potassium and zirconium) is possible only if the conditions are such that the mixtures of compounds that are formed possess a 3 : 1 ratio of iodate groups to potassium. Such compounds can be characterized by the ratios $K : Zr : IO_3 = 1 : 1 : 3$, $2 : 1 : 6$, $3 : 1 : 9$, $4 : 1 : 12$, etc.

It is possible to make the proper selection on the basis of the results presented in Table 3.

The data given in this table show that the first variant (with the ratio $K : Zr : IO_3 = 1 : 1 : 3$) is excluded, inasmuch as the precipitates containing 3 iodate groups for 1 atom of zirconium do not contain any potassium. Compounds containing 12 and more iodate groups for 1 atom of zirconium should be excluded, inasmuch as not one of the obtained precipitates contained more than 9 iodate groups and more than 3 atoms of potassium for 1 atom of zirconium (even at maximum saturation of the solution with potassium iodate).

In the precipitates containing 7 and 8 iodate groups for 1 atom of zirconium the ratios between potassium and zirconium are expressed by fractional values; consequently these precipitates can be considered as being mixtures.

An examination of the numerical analysis results leads to the conclusion that on long standing the triiodate is converted only into two compounds, the hexaiodate and the enaiodate. The first compound contains 2 atoms of potassium, while the second compound contains 3 atoms of potassium (Table 3).

Zirconium hexaiodate and enaiodate can be depicted as being either binary salts or as being complex compounds.

Observations show that both compounds are readily hydrolyzed by water with transformation into hydroxy compounds. When dissolved in nitric acid the hexaiodate and enaiodate decompose into simple ions, consequently the subsequent addition of sufficient potassium iodate to the nitric acid solution results in the separation of the triiodate in the precipitate.

Taking into consideration the properties of the precipitates, it seems expedient to depict them as being binary salts – $Zr(IO_3)_4 \cdot 2KIO_3$ (hexaiodate) and $Zr(IO_3)_4 \cdot 3KIO_3 \cdot 2HIO_3$ (enaiodate).

SUMMARY

1. Freshly precipitated zirconium iodate is not stable. On long standing with the mother liquor the precipitate reacts with potassium iodate and iodic acid to yield the hexaiodate and the enaidoate.

2. In the formation of the hexaiodate and enaiodate the precipitates are transformed from the amorphous state to the crystalline state. The rate of transformation to the crystalline state is accelerated with increase in the concentration of potassium iodate in the solution (for nitric acid solutions) or with increase in the concentration of iodic acid and potassium iodate (in the precipitation of zirconium from water solutions of the nitrate).

3. The hexaiodate, devoid of any enaiodate as impurity, is formed only in very narrow concentration limits of potassium iodate in the solution (the limits change with change in the acidity).

The enaiodate is formed at high concentrations of iodate ions in the solution and at favorable relative concentrations of iodic acid and potassium iodate.

Mixtures of the hexaiodate and enaiodate are most frequently found in the precipitates, the relative amounts of which change with change in the concentrations of iodate ions and potassium in the solution.

4. Independent of the average composition of the mixtures, the amount of iodate groups in them with respect to potassium is expressed by a constant value, equal to 3, which value is conditioned by the composition of the hexaiodate and enaiodate present in the mixture.

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NIOBATES AND TANTALATES OF ALKALI EARTH METALS

I. Metaniobates and Metatantalates of Calcium, Strontium and Barium

V. A. Pchelkin, A. F. Efimov and A. V. Lapitsky

The first information on the preparation of anhydrous metaniobates of the alkali earth elements was published in 1875 [1]. The anhydrous metatantalates of the alkali earth metals were synthesized at a considerably later date [2,5]. The authors of the indicated papers make no mention of studying the properties of the given compounds.

We set ourselves the task of synthesizing the metaniobates and metatantalates of the alkali earth metals, and also of studying some of their properties.

EXPERIMENTAL

Starting materials. The pentoxides of niobium and tantalum were obtained by the method of separating the technical mixture. Chemically pure gades of calcium, strontium and barium carbonates were used.

Preparation of the metaniobates and metatantalates of the alkali earth metals. The metaniobates and metatantalates of calcium, strontium and barium were obtained by fusion of equimolecular amounts of niobium (or tantalum) pentoxide and the corresponding carbonate of the alkaline earth metal. In order to accelerate the fusion, potassium fluoride was used as flux, added in an amount equal to 0.1 weight part on the weight of the mixture. The finely pulverized mixtures were poured into crucibles, which were then heated in the furnace for a period of 3 hours at 1200°. A white crystalline substance was obtained after fusion.

In order to remove potassium fuloride the substance was pulverized and treated with water. After drying at 120° the salt was analyzed for the amount of niobium (or tantalum) pentoxide and metal oxide. Weighed samples of the salts were fused with an excess of ammonium hydrosulfate in porcelain crucibles. After complete cooling, the formed transparent melts were leached with a solution of ammonium oxalate. The insoluble deposits contained the sulfates of the alkaline earth metals.

After removal of the sulfates, the oxalate solutions were heated on the water bath and treated with a freshly prepared 2 % tannin solution. The niobates were precipitated from weakly alkaline solution, while the tantalates were precipitated from weakly acidic solution. The analysis results obtained for the salts are given below.

Analysis of calcium metaniobate

Weight of substance 0.2566 and 0.1470 g

Found %: Nb_2O_5 81.98, 82.00; CaO 17.26, 17.20. $Ca(NbO_3)_2$. Calculated %: Nb_2O_5 82.61; CaO 17.39.

Analysis of strontium metaniobate

Weight of substance 0.2462 and 0.2256 g

Found %: Nb_2O_5 71.96, 71.58; SrO 27.54, 27.38. $Sr(NbO_3)_2$. Calculated %: Nb_2O_5 72.33; SrO 27.67.

Analysis of barium metaniobate

Weight of substance 0.1826 and 0.1830 g

Found %: Nb_2O_5 63.20, 63.21; BaO 36.34, 36.30. $Ba(NbO_3)_2$. Calculated %: Nb_2O_5 63.49; BaO 36.51.

Analysis of calcium metatantalate

Weight of substance 0.3044 and 0.3144 g

Found %: Ta_2O_5 88.69, 88.53; CaO 11.65, 11.42. $Ca(TaO_3)_2$. Calculated %: Ta_2O_5 88.75; CaO 11.25.

Analysis of strontium metatantalate

Weight of substance 0.2866 and 0.1516 g

Found %. Ta_2O_5 80.18, 81.13; SrO 19.88, 19.78. $Sr(TaO_3)_2$. Calculated %. Ta_2O_5 80.97; SrO 19.03.

Analysis of barium metatantalate

Weight of substance 0.1614, 0.2218 g

Found %. Ta_2O_5 74.66, 74.39; BaO 25.59, 26.08. $Ba(TaO_3)_2$. Calculated %. Ta_2O_5 74.29; BaO 25.71.

The chemical analysis results show that we had obtained the anhydrous metaniobates and metatantalates of the alkaline earth metals, of which the majority had been obtained for the first time.

In order to be sure that the reaction had gone to completion in the heating of mixtures of niobium (or tantalum) pentoxide with the carbonates of the alkaline earth metals, we made X-ray phase analyses of the mixtures, which in all cases showed the presence of a single phase.

Properties of the metaniobates and metatantalates of the alkaline earth metals. All of the investigated salts have high melting points. In the present study we conducted experiments to determine the volatility of all of the metaniobates and metatantalates of the alkaline earth metals.

The experimental procedure was described earlier. The volatility studies were made at atmospheric pressure and in vacuum. The duration of heating was 6 hours. The experimental results show that the investigated compounds possess thermal stability and are nonvolatile even in vacuum.

This property of the indicated salts can be understood when their properties are compared with the properties of the earlier described metaniobates and metatantalates of the alkali metals [3].

It should be mentioned that the metaniobates of calcium, strontium and barium change their color when heated in vacuum, acquiring a light gray cast. It has already been mentioned by us that a similar phenomenon is observed when the anhydrous metaniobates of the alkali metals are heated in vacuum.

As was indicated, the thermal stability and high melting points of these salts can be explained on the basis of the monolithic character of the ions NbO_3^{-1} and TaO_3^{-1} [4]. The properties of the metaniobates and metatantalates of calcium, strontium and barium can be considered in an analogous manner. Here also the monolithic metaniobate and metatantalate ions fail to exert a polarizing influence on the calcium, strontium and barium ions. Because of their nature, the latter ions fail to exert any appreciable polarizing action on the corresponding anion. This fact determines the character of the bond as being ionic, and conditions the high melting point and nonvolatility of the compounds. As was shown in the preliminary experiments, all of the metaniobates and metatantalates of the alkaline earth metals have a low solubility in water.

We studied the conductance of saturated solutions of all of the above indicated salts at 20°. The saturated solutions were prepared with double distilled water. The specific conductance was calculated with the aid of the formula $\chi = KW$, where K is the vessel constant, $W = \frac{1}{R_{soln.}}$.* The measurement results are given in the table.

TABLE
Specific Conductance of Saturated Solutions of Anhydrous Metaniobates and Metatantalates of Calcium, Strontium and Barium at 20°.
(Vessel Constant 0.4433)

Salt	Specific conductance (ohm^{-1} cm^{-1})
$Ca(NbO_3)_2$	$1.22 \cdot 10^{-5}$
$Sr(NbO_3)_2$	$2.06 \cdot 10^{-6}$
$Ba(NbO_3)_2$	$3.81 \cdot 10^{-6}$
$Ca(TaO_3)_2$	$2.14 \cdot 10^{-5}$
$Sr(TaO_3)_2$	$0.99 \cdot 10^{-5}$
$Ba(TaO_3)_2$	$1.42 \cdot 10^{-5}$

Attention is directed to the fact that barium metaniovate and barium metatantalate possess a greater solubility than do the corresponding strontium salts, the latter possessing an extremely low solubility. On the other hand, it is a striking fact that the metatantalates show a greater solubility than do the metaniobates. The absence of literature data on the mobility of the ions NbO_3^{-1} and TaO_3^{-1} makes it impossible to calculate the solubility values for the investigated salts from the specific conductance data.

SUMMARY

1. The anhydrous metaniobates of strontium and barium and the metatantalates of calcium, strontium and barium have been synthesized.

2. It was established that all of the indicated salts and calcium metaniobate are thermally stable and do not possess any noticeable volatility even in a vacuum.

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* The specific conductance of water was $1.4 \cdot 10^{-6}$ ohm^{-1} cm^{-1}.

3. The specific conductance of saturated solutions of the anhydrous metaniobates and metatantalates of the alkaline earth metals was measured at 20°.

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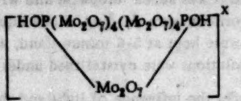
STRUCTURE OF PHOSPHO-9-MOLYBDIC (LUTEOPHOSPHOMOLYBCID) ACID

E. A. Nikitina and O. N. Sokolova

The question of the basicity and structure of the inner sphere of unsaturated heteropoly acids with the ratio $RO_x : NeO_y = 1 : 9$ is completely obscure; there are indications in the literature that these acids are six ten and twelve basic [1]. In 1953 Dawson [2], using X-ray structure analysis and electronographic methods, made an attempt to determine the structure of potassium luteophosphotungstate, however, the carefully executed work made it possible to establish only the position of the tungsten atoms in thes salt; as regards the distribution of the oxygen atoms and in part of phosphorus, for the solution of this problem Dawson depended to a considerable degree on the earlier work of Keggin [3]; Dawson was simply unable to determine the position of the potassium ions and the water molecules. It should be mentioned that an analysis of the compound used in the investigation is not given in Dawson's paper, and the unverified gross formula assigned to it is $3K_2O \cdot P_2O_5 \cdot 18WO_3 \cdot 14H_2O$.

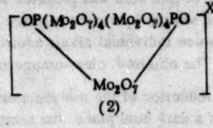
One of the positive results of the investigation is Dawson's conclusion that the heteropoly acids of the 9th series are binuclear complexes. As a result, using X-ray structure analysis and electronographic methods, Dawson confirmed that general configuration of complex molecules that is also assigned to them from coordination studies. However, all of the former problems relating to the structure of heteropoly acids of the 9th series, like the matter of their basicity, the structure of the inner sphere, the character of the addenda, etc., remained unsolved.

A method was developed by us for the preparation of luterophosphomolybdic acid [4]; the possibility of having any desired amount of this compound at our disposal permitted us to study the question of its structure. The syntheses of the sodium, potassium and ammonium salts show that the compound is hexabasic, the synthesis of the guanidine salt indicates that it is dodecabasic; the determination of the equivalent conductance when luteophosphomolybdic acid is neutralized with sodium hydroxide indicates that it is octabasic. As a result, the question of the basicity of luteophosphomolybdic acid remains debatable. For its soltuion and in order to elucicate the structure of the inner sphere the only idea that could serve as a guide in our investigation was the coordination study. In accord with this theory two structural formulas are possible for luteophosphomolybdic acid; in accord with the first formula the heteropoly acid is decabasic and functions as a hydroxy compound; the second formula depicts it as being a dodecabasic oxo acid; in both cases the inner sphere of the compound is thought to be a binuclear complex.



$$\left[HOP(Mo_2O_7)_4(Mo_2O_7)_4POH \; Mo_2O_7\right]^{X}$$

(1)



$$\left[OP(Mo_2O_7)_4(Mo_2O_7)_4PO \; Mo_2O_7\right]^{XII}$$

(2)

EXPERIMENTAL

Our experiments on the potentiometric titration of luterophosphomolybdic (subsequently we will write it as lpm) acid solutions with solid sodium hydroxide were conducted in the presence of a quinhydrone electrode. During the titration process the latter dissolved; the minimum conductance was not attained even on adding 40 equivalents of alkali. In subsequent work we obtained soluble sodium salts of lpm acid by the method of gradual replacement of all of the possible hydrogen ions in the acid molecule, and investigated the obtained compounds.

We were able to establish that lpm acid is a strong acid: the pH of a 0.01 M solution, determined by the colorimetric method, is 0.5.

As is known, the heteropoly acids are decomposed by alkalies, as a result of which the danger exists that the direct action of alkali on lpm acid will cause the decomposition of the latter. Actually, when the calculated amount of alkali is rapidly added in one dose the solution warms up considerably and a cloudiness appears due to the precipitation of molybdic acid. A sample of the solution showed the presence of saturated phosphomolygdic acid, i.e., partial decomposition had taken place. When the alkali is added slowly by equivalents but without cooling, it was noted that partial transformation of lpm acid into saturated phosphomolybdic acid had taken place.

As a result of the performed orientating experiments it was found that it is possible to avoid the decomposition of the heteropolyanion if 10 N sodium hydroxide solution is slowly (dropwise) added to a 40-45 % solution of lpm acid at a temperature not exceeding 30°.

The synthesis of the sodium salts was carried out in the following manner: the solution of lpm acid was prepared and analyzed for the total amount of the oxides P_2O_5 + MoO_3; then to a known weight of such a solution the calculated amount of standard sodium hydroxide solution was slowly added in portions with good mixing, each portion being equal to one equivalent; successive portions were added at 2-3 minute intervals. During neutralization the solution was cooled with a mixture of ice and water, and its temperature was maintained at 20-30°. Under these conditions no evidence of decomposition was observed.

The isolation of crystalline salts from the obtained solutions was associated with great difficulties. When concentration of the clear orange-yellowish solutions was attempted by boiling or by evaporation on the water bath at 65-70° it was established that the complex undergoes decomposition in both cases. It was noticed that the stability of the salt solutions increases in accord with increase in the number of equivalents of alkali added, but not in a single case was it possible to use the inidcated concentration methods without incurring some decomposition. Some experiments were performed on evaporation of the salt solutions in vacuum (water suction pump) at a temperature of 65-70°. At first the evaporation proceeded satisfactorily, but with increase in the concentration of the solution it was noticed that sirupy solutions began to form, these solutions later congealing into dense vitreous masses. We finally had to settle on the isothermal evaporation ot the salt solutions in desiccators over sulfuric acid at 18-20°. But even in the given instance the isolation of individual crystalline compounds proved to be an extremely rare occurrence. For the investigations it was found necessary to isolate the crystallline compounds in the presence of mother liquor.

In subsequent work the water medium was replaced by alcohol. It was established that lpm acid is readily soluble in alcohol; a 40-45 % alcohol solution of the acid is stable for long periods of time (about a month), provided there are no significant variations in the storage temperature.

The monosubstituted sodium salt of lpm acid was prepared in alcohol solutions in a manner analogous to its synthesis in water medium; the obtained salt solution was more stable than the corresponding water soltuion.

Next the problem reduced itself to evaporation of the alcohol without incurrring decomposition of the salt. Attempts to use the water bath for this purpose failed to give positive results. Attempts were made to evaporate the alcohol solutions at room tempeature; for this purpose the salt solutions were poured in large watch glasses and allowed to stand on the bench. The disadvantages of this method were the vigorous reduction of hexavalent molybdenum by the heteropoly anion; consequently, we finally decided to use the method of isolating the salt crystals form aqueous solutions.

A 40-45% solution of lpm acid was prepared and to it was added, dropwise and with constant sitrring, the calculated amount of standard sodium hydroxide solution in portions corresponding to one equivalent on the amount of acid taken; the intervals between individual alkali additions were kept at 5-6 minutes and, as was indicated above, the solutions were cooled. The obtained clear orange salt solutions were cyrstallized under isothermal conditions.

In order to avoid reduction of the molybdenum under the influence of light and sharp temperature changes, the desiccators were kept in a dark cool place, the temperature of which changed but slightly up to the separation of a sufficient amount of crystals, inasmuch as on attaining a certain degree of concentration a slight movement of the vessel or stirring of the solution toward the end of evaporation was sufficient to cause complete solidification (super saturation).

As the result of prolonged and exact operation with this method we wereable to isolate all of the sodium salts of lpm acid, ranging from the mono- to the dodecasubstituted compound.

The analysis results for the obtained sodium salts of lpm acid are given in Table 1, as well as the pH measurements of the mono-, hexa- and dodecasubstituted salt solutions, determined by the colorimetric method.

To determine the amount of water about 1 g of the salt was dried at 100-110° for 1hour, then heated up to 300°, maintained at this temperature for about 1.5 hours and then carefully ignited in the burner flame for 2-3 minutes. The loss in weight corresponded to the water content.

P_2O_5 and Na_2O were determined in the salts by the earlier described method [6]. MoO_3 was determined by difference.

When alakli was added in an amount equal to 13 equivalents per mole of acid the color of the latter solution changed from orange to pale green; in accord with increase in the degree of evaporation in the desiccator the color became somewhat more intense, but it retained a greenish cast even after the addition of hydrogen peroxide. After stand ing for a short time white crystals began to appear on the surface of the solution, and soon after this the solution was transformed into a dense mass of ill-defined crystals. When the mass was filtered on a Nutsch filter a yellowish-green filtrate was obtained, while the precipitate was a mixture of white and pale green clumps, the separation of which did not appear possible.

The obtained compound was analysed for the amount of H_2O, P_2O_5 and Na_2O. The analysis results are given in Table 2.

TABLE 1

Analysis Results for the Sodium Salts of Lpm Acid

Degree of substitution in the salt	Found H_2O (in %)	Found based on anhydrous composition (in %)			Calculated from the formula (in %)			pH of the solution (0.01 M)
		Na_2O	P_2O_5	MoO_3	Na_2O	P_2O_5	MoO_3	
Monosubstituted	9.71	1.21	5.13	93.66	1.12	5.14	93.74	~ 1
	10.22	1.17	5.15	93.68				
Disubstituted	10.13	2.33	5.06	92.61	2.22	5.08	92.70	–
	17.38	2.29	5.08	92.63				
Trisubstituted	9.67	3.20	5.05	91.75	3.29	5.02	91.63	–
	16.27	3.39	5.00	91.61				
Quadrisubstituted	17.73	4.29	4.96	90.75	4.34	4.97	90.69	–
	16.67	4.40	4.91	90.69				
Pentasubstituted	11.12	5.42	4.90	89.68	5.37	4.92	89.71	–
	10.79	5.31	4.83	89.86				
Hexasubstituted	9.82	6.23	4.83	88.94	6.37	4.86	88.77	~ 4.5
	11.30	6.35	4.84	88.81				
Heptasubstituted	18.03	7.24	4.81	87.95	7.35	4.81	87.84	–
	10.41	7.61	4.90	87.49				
Octasubstituted	16.84	8.26	4.70	87.04	8.32	4.76	86.92	–
	16.28	8.31	4.72	86.97				
Nonasubstituted	12.20	9.37	4.75	85.88	9.26	4.71	86.03	–
	17.78	9.50	4.77	85.73				
Decasubstituted	10.54	9.95	4.68	85.37	10.19	4.67	85.14	–
	11.42	10.35	4.60	85.05				
Undecasubstituted	11.47	11.23	4.66	84.11	11.09	4.62	84.29	–
	11.79	11.31	4.67	84.02				
Dodecasubstituted	16.48	11.80	4.53	8.67	11.98	4.57	83.45	~ 6.5
	17.55	11.91	4.50	8.59				

TABLE 2

Analysis of the Compound Obtained on Adding 13 Equivalents of Alkali to 1 Mole of Lpm Acid

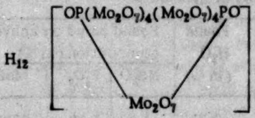
Compound	Found (in %)	Found based on anhydrous composition (in %)	Calculated from the formula (in %)	
			$3Na_2O \cdot P_2O_5 \cdot 14MoO_3$	$2Na_2O \cdot P_2O_5 \cdot 14MoO_3$
H_2O	11.63	–	–	
P_2O_5	5.38	6.09	6.06	5.43
Na_2O	5.92	6.70	7.96	6.22
MoO_3	–	87.21	85.98	88.35

According to the given analysis, the obtained crystals are the trisubstituted salt of phospho-7-molybdic acid with the disubstituted salt of the same series being present as impurity.

Apparently, the addition of one equivalent of alkali to a solution of dodecasubstituted sodium luteophosphomolybdate leads to the decomposition of the latter with the formation of unsaturated heteropolyaacid salts less rich in molybdenum.

The fact that we were able to prepare highly substituted and readily soluble sodiums salts of lpm acid confirmed the validity of the coordination theory, which theory admits the multibasicity of heteropoly acids also with respect to unsaturated compounds, in which number lpm acid is included.

On the basis of the performed synthesis the structure of the hydroxy compound should be rejected and it should be assumed that lpm acid, being dodecabasic, is an oxo compound, having a structure corresponding to the formula



$$H_{12}\left[\begin{array}{c}OP(Mo_2O_7)_4(Mo_2O_7)_4PO\\ Mo_2O_7\end{array}\right]$$

As a result, it was established that luteo acids with phosphorus as the complexing agent, as was to be expected from the coordination theory, are dodecabasic and not hexabasic, as many foreign investigators had thought up to the present time.

Viscosimetric study of sodium salt solutions of lpm acid. We studied the densities and viscosities of different concentrations of the mono-, hexa- and dodecasubstituted sodium salt solutions of lpm acid at 20°.

The analysis results for the salts used in the investigation are given in Table 3.

TABLE 3
Analysis Results for Sodium Luteophosphomolybdate

Salt composition	Found, based on anhydrous composition (in %)			Calculated from the formula (in %)		
	Na_2O	P_2O_5	MoO_3	Na_2O	P_2O_5	MoO_3
Monosubstituted	1.17	5.15	93.68	1.12	5.14	93.74
Hexasubstituted	6.23	4.83	88.94	6.37	4.86	88.77
Dodecasubstituted	11.80	4.53	83.67	11.98	4.57	83.45

The investigations were carried out in a glass thermostat equipped with a stirrer. Glass pycnometers, having approximate volumes of 1.3 and 0.25 ml, were used for the specific gravity determinations. Ostwald viscosimeters were used to study the viscosities of the solutions.

The viscosity was calculated from the formula $\eta = \eta_0 \frac{dt}{d_0\, t_0}$, where η_0 is the viscosity of water at the investigated temperature in poises, d and t are the specific gravity and rate of flow for the investigated solution, while d_0, t_0 are the same values for water (Table 4, Figures 1 and 2).

For orientation purposes in connection with the preparation of solutions for studying the viscosities of the salts, we determined the solubility of the mono-, hexa- and dodecasubstituted salts in water at 20°.

The solubilities of the salts were based on the anhydrous compound (in %): for the monosubstituted salt 68.81, for the hexasubstituted 67.26, and for the dodecasubstituted 68.25.

From the presented graphs it can be seen that the viscosity isotherms appear as smooth lines. The absolute viscosity values for the salt solutions are less than for the free acid; the solubility values also differ from the solutility of the acid and differ between themselves; the pH values of the salt solutions are different. This permits drawing the conclusion that all of the obtained sodium salts of lpm acid are individual chemical compounds.

The viscosity and specific gravity values for the mon-, hexa-, and dodecasubstituted salts are extremely close. This proximity in the properties of salts with different degrees of substitution permits considering the heteropoly compounds in some cases exhibit the properties of compounds of the daltonide type, while in other properties their berthollide nature is more clearly defined.

In the work [5] it was established that heteropoly acids are two-layered complexes. The complexing agent coordinates 6 nonequivalent oxygen ions, which in their turn are surrounded in lpm acids by MoO_3 radicals. Apparently, the MoO_3 radicals are connected between themselves by a common oxygen bond, as a result of which Mo_2O_7 radicals are formed. These oxygen bonds in the case of molybdenum are more stable than they are in the case where they are found in the inner sphere of WO_3 radicals. Actually, during the gradual addition of KOH to silicotungstates the WO_3

groups were removed one at a time from the inner sphere; in the case of adding one equivalent of NaOH to the dodecasubstituted sodium luteophosphomolybdate we obtained the cleavage of two MoO_3 groups.

TABLE 4

Specific Gravity and Viscosity of Sodium Luteophosphomolybdate Solutions

Salt Composition	Solution concentration (in %)		d	$\eta \cdot 10^2$
	Weight	Molal		
Monosubstituted	24.92	0.2157	1.25	1.42
	37.47	0.3887	1.42	1.87
	51.31	0.6790	1.68	3.10
	61.19	1.0164	1.94	6.48
	66.88	1.2981	2.13	10.43
Hexasubstituted	27.61	0.2346	1.28	1.51
	37.21	0.3642	1.41	2.06
	52.64	0.6807	1.70	3.41
	60.38	0.9310	1.90	5.70
	63.33	1.0537	1.98	5.87
Dodecasubstituted	25.51	0.1981	1.25	1.33
	37.72	0.3499	1.45	1.92
	44.37	0.4602	1.56	2.32
	59.02	0.8280	1.88	5.81
	64.39	1.0374	2.01	8.27

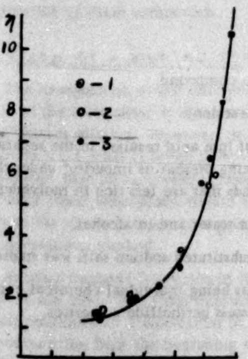


Fig. 1. Curve for the relationship between viscosity and salt concentration in the solution.

1 - Monosubstituted, 2 - Hexasubstituted, 3 - Dodecasubstituted

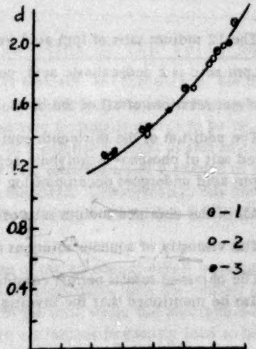


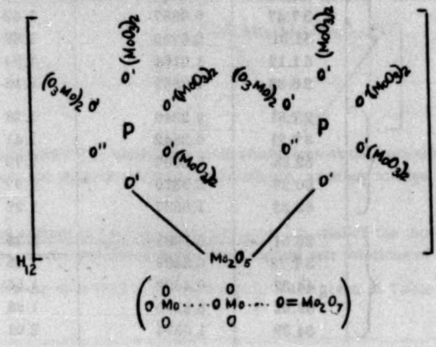
Fig. 2. Curve for the relationship between specific gravity and salt concentration in the solution.

1 - Monosubstituted, 2 - Hexasubstituted, 3 - Dodecasubstituted

The first manifestation of difference in behavior for the coordinated groups WO_3 and MoO_3 should be attributed to the structure of the tungsten and molybdenum ions themselves. Apparently, the inner sphere radicals MoO_3 or

WO_3 are arranged in the inner sphere of heteropoly acids in a manner similar to the arrangement of the oxygen atoms in potassium dichromate. This fact makes it possible to give the structural formula for lpm acids. According to Pfeiffer we retain the nonequivalent oxygen atoms in this formula.

Under the influence of alkali the bond between the oxygen and two MoO_3 groups is broken; either the MoO_3 groups are removed by single cleavage from the number surrounding both central ions or the bridge is destroyed, it is impossible to definitely say which is true inasmuch as it is necessary to study the propetries of the phospho-7-molybdates in order to find the answer.



Two oxygen ions, surrounding the central ion, create the bridge bond; apparently, because of such a bond character the luteo acid is considerably less stable than the saturated acid.

SUMMARY

1. The 12 sodium salts of lpm acid were obtained for the first time.

2. Lpm acid is a dodecabasic acid, possessing the structure of an oxo compound.

3. Water solutions of all of the obtained sodium salts show an acid reaction.

4. The addition of the thirteenth equivalent of NaOH to a solution of lpm acid resulted in the separation of the trisubstituted salt of phospho-7-molybdic acid with the disbustituted salt being present as impurity, under these conditions the lpm acid undergoes decomposition with the formation of compounds that are less rich in molybdenum.

5. All of the obtained sodium salts of lpm acid are readily soluble in water and in alcohol.

6. The viscosity of aqueous solutions of the mono-, di- and dodecasubstituted sodium salts was studied at 20°.

7. The obtained results permit considering all of the obtained salts as being individual chemical compounds; it should also be mentioned that the investigated heteropoly compounds possess berthollide properties.

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COMPOSITION OF DIFFICULTLY SOLUBLE NICKEL COMPOUNDS PRECIPITATED BY ALKALI FROM SULFATE SOLUTION, AND THEIR STANDARD ISOBARIC POTENTIALS OF FORMATION

A. L. Rotinyan, V. L. Kheifets, E. S. Kozich, and E. N. Kalnina

It is known that nickel ions, as well as many other metallic ions, under the proper conditions form difficultly soluble hydroxides, basic salts and even more complex compounds. However, despite the large number of researches on the subject the composition and conditions for the formation of difficultly soluble nickel basic salts have not been established up to now. Thus, for example, Britton [1] found that 1.66 equivalents of alkali is required to precipitate all of the nickel from a 0.025 M solution, which fact is evidence that the basic salt is precipitated. On the other hand, Fialkov and Akselrud [2,3] consider the nature of their experimental results as being due to the formation of pure nickelous hydroxide in all of the concettration intervals studied by them. Rotinyan and Zeldes [4] showed that, at low concentrations of nickel sulfate in the potentiometric titration of the solution with alkali the pure nickelous hydroxide $Ni(OH)_2$ is formed, while at the same time for higher concentrations of $NiSO_4$ the solid phase consists of basic salts. Singley and Carriel [5] found that basic compounds are formed when nickel is precipitated by alkali from nickel chloride, nitrate, or sulfate solutions, these compounds with further elevation of the pH undergoing transition into the pure hydroxide.

According to the observation made by Bagno [6], the difficultly soluble nickel compound, precipitated from nickelous chloride solution by a mixture of NaOH and Na_2CO_3, undergoes a change in composition with time. The CO_3'' ions, first found in the precipitate, are replaced by hydroxyl ions with the passage of time.

In the present study we set ourselves the task of establishing the composition of difficultly soluble nickel compounds, elucidate the conditions for their formation, and compute where possible the standard isobaric potentials for the formation of these compounds.

Selection of a method for determining the composition of the solid phase

The composition of the solid phase can be determined by several methods. At first glance, the most reliable composition of the solid phase is obtained by direct chemical analysis of the difficultly soluble compound, separated from its equilibrium solution. However, on closer examination this method very frequently proves to be inaccurate. Actually, if the solid phase is found in equilibrium with the solution only in a definite interval of salt activities and solution acidities, then on removing it from the mother liquor by washing with distilled water a change in the composition of the solid phase takes place toward the formation of a more basic compound. Consequently, this method is adaptable only in the case where constancy in the composition of the solid phase during washing has been established by some other independent method.

Another method [1] consists in the potentiometric determination of the amount of alkali necessary to precipitate all of the metal ions from solution. Calculation of the solid phase composition from the number of equivalents of alkali consumed for 1 equivalent of metal gives a true value only in the case where the precipitate retains a constant composition from the beginning to the end of the titration. Such a situation frequently fails to hold true in practice [7].

It is possible to determine the most trustworthy composition of the solid phase from the slope values for the relation pH vs. log metal salt activity in solution, with a large number of experimental points being plotted [7].

For this method it is necessary to know the pH values of the solutions in equilibrium with the solid phase at different salt activities. The hydrogen ion concentration in the solution found in equilibrium with the solid phase can be obtained by measuring the pH of the solution, brought to a state of visible turbidity by the addition of an alkaline reagent and held in order to attain equilibrium (Gromov • [8]).

• At low salt concentrations the method of Gromov has the disadvantage that a considerable portion of the salt may be lost in the formation of turbidity, and consequently its equilibrium concentration will be substantially different from the initial concentration, which concentration is used in the calculations.

The method of Akselrud and Fialkov [3], in accord with which the hydroxide (or basic salt) is precipitated separately, filtered and then brought into equilibrium with the salt solution (the equilibrium concentration of the salt is analyzed separately), gives the same physical value for the pH. Therefore, it is natural for the experimental data obtained by methods [3] and [8] to coincide with each other.

Other methods, by some means or other, fix the pH at the beginning of solid phase formation in the process of adding alkali to the solution. The initiation of solid phase formation can be detected by the inflection on either the potentiometric or conductometric titration curves, and also from polarographic measurement data [9,10].*

This group of methods usually requires fairly rapid experimental execution, as a result of which the solid phase may consist not of compounds in equilibrium with the solution but of difficultly soluble pseudoequilibrium compounds, for which the pH of formation differs from that of the equilibrium compounds.

The fact that the pH values determined by methods [8] and [3] at times are higher than the values obtained in the second group of methods is apparently due to the above situation.

To determine the composition of the solid phase we used in the present work the earlier described calculation method based on the slope coefficient values of the linear functions pH−log a ± [7]. To verify the obtained results we developed still another method for determining the composition of the deposited solid phase, based on measurement of the electrical conductivity of the coexistent solution. A detailed description of this method is given below.

EXPERIMENTAL

a) Measurement of the pH of formation of the hydroxide and basic salts of nickel by the potentiometric method. The pH values of the solutions coexisting with the solid phase were determined by both method [8] and by the potentiometric method [11].

It should only be emphasized that the potentiometric titration curves are taken in such a manner that each point is the result of measuring the established value of the electromotive force (change in e.m.f. < 1mV after 10-15 minutes). Reproducibility of the results was within ±0.1 pH. The reagents used were carefully purified. Standard 0.1 N NaOH was used for the titrations.

The pH values corresponding to initial solid phase formation are given in the table. In the table are also given the pH values of the solutions in equilibrium with the solid phase, determined by the method of Bromov. These values for the coordinates pH−log a± are depicted in Fig. 1. First of all it should be mentioned that the obtained results are in excellent agreement with the literatuare data [3,4], with the exception of the experiments performed by Gayer and Garrett [12], in which in dilute nickel chloride solutions the slope coefficient of the relation pH−log a ± proves to be 0.5 (i.e., the solid phase consists of pure nickel hydroxide, which agrees with our data) but the absolute pH values in their experiments are shifted by approximately a pH unit when compared with the values depicted in Fig. 1. Apparently, this divergence is caused by some systematic error hidden in the measurements of Gayer and Garrett. Further, it can be seen from Fig. 1 that at concentrations of nickel sulfate up to approximately 0.1 M the compound found in equilibrium with the solution (top curve) is the pure hydroxide (slope coefficient of the straight line is 0.5). At concentrations of nickel sulfate ranging from ~ 0.1 to ~ 1.0 the basic salt of composition $3NiSO_4 \cdot 4Ni(OH)_2$ is found in equilibrium with the solution. The composition of this basic salt is determined from the slope of the linear function pH−log a ± according to the formula

$$pH = \frac{\Delta Z^0\,\text{basic}}{2.3nyRT} - \frac{y+bx+dx}{ny}\log a\pm - \frac{1}{ny}\log\frac{b^{(y+bx)}d^{xd}}{\left(\frac{b}{b^{b+d}}\cdot\frac{d}{d^{d+b}}\right)^{y+bx+dx}} - \log K_w \qquad (1)$$

the derivation of which was given earlier [7].

(Here $\Delta Z^0_{\text{basic}}$ − standard isobaric potential of forming the basic salt in accord with the scheme:

$$(y+bx)\,Me^{n+} + dx\,A^{m-} + ny\,OH' \rightleftharpoons x[Me_bA_d]\,y[Me(OH)_n].$$

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* The last method, recently proposed by Kovalenko, is to be preferred when the measurements are made in dilute solutions. Kovalenko determined the moment of initial hydroxide formation and the pH corresponding to it from the decrease in the metal diffusion current, taking a series of polarograms at different pH values.

If the titration is made, given the dropping mercury cathode diffusion potential, then the curve, constructed by Kovalenko from a number of polarograms, is obtained directly.

$a_\pm$ – mean salt activity in the solution, K_W – ionic product of water).

TABLE

The Influence of Nickel Sulfate Concentration on the pH of Solutions Coexisting with the Solid Phase

Nickel concentration		$\gamma_\pm$	$a_\pm$	pH potentiometrically determined at		pH determined by the method of Gromov at 20°
g/liter	M			20°	50°	
0.10	0.0017	0.66	0.00112	7.94	7.04	7.66
0.15	0.0025	0.60	0.00150	7.90	6.86	7.87
0.20	0.0034	0.55	0.00187	7.85	6.82	7.78
0.30	0.0051	0.49	0.00249	7.77	6.80	7.70
0.40	0.0068	0.46	0.00309	7.58	6.68	7.62
0.49	0.0083	0.43	0.00355	–	–	7.53
0.50	0.0085	0.42	0.00361	7.61	6.62	7.63
0.60	0.0102	0.40	0.00413	7.58	6.45	7.56
0.70	0.0119	0.38	0.00458	7.44	6.56	7.56
0.80	0.0136	0.37	0.00503	7.36	6.52	7.55
0.90	0.0153	0.35	0.00543	7.34	6.46	7.48
0.96	0.0163	0.34	0.00562	–	–	7.48
1.0	0.0170	0.34	0.00578	7.24	6.42	7.52
1.0	0.0170	0.34	0.00578	–	–	7.38
1.5	0.0255	0.29	0.00739	7.10	6.38	–
1.88	0.0320	0.26	0.00848	–	–	7.38
2.0	0.0341	0.26	0.00886	7.08	6.32	7.30
2.14	0.0364	0.26	0.00937	–	–	7.38
3.0	0.0511	0.23	0.01175	6.92	–	–
5.0	0.0852	0.18	0.01533	6.78	5.94	7.28
10	0.1704	0.12	0.02044	6.51	5.70	7.17
20	0.3408	0.075	0.02556	6.41	5.36	6.98
30	0.5146	0.065	0.03345	6.15	5.16	6.88
40	0.6815	0.055	0.03748	6.10	5.14	6.77
50	0.8519	0.050	0.04259	6.04	4.98	6.72
60	1.0223	0.045	0.04600	5.84	4.94	6.67

b) Study of the composition of basic salts by the electrical conductivity method. We will examine the case where the addition of alkali to a nickel sulfate solution results in the formation of a difficultly soluble compound in accord with the reaction

$$(x + y)\,NiSO_4 + 2yNaOH = x\,NiSO_4 \cdot yNi(OH)_2 + yNa_2SO_4. \qquad (2)$$

To perform the experiment we chose such concentrations of salt and alkali that, first, the conductivity of the mixed solution as a first approximation was additively composed of the conductivities of the individual component solutions and, second, that in the selected concentration interval the change in the specific conductance of the solution was proportional to the salt concentration.

With progress of reaction (2) the conductivity of the solution should drop due to decrease in nickel sulfate concentration and simultaneously it should rise due to the formation of sodium sulfate. The change in the specific conductance of the solution during solid phase formation is influenced by both factors.

If the experiment is conducted in such a manner that to a constant volume of nickel sulfate solution of concentration C_1 there is added V ml of alkali solution of concentration C_2, the solution made up to constant volume W with distilled water, next filtered and the specific conductance of the filtrate determined, then, in accord with the equation for the reaction, the change in nickel sulfate concentration is expressed by

$$\Delta C_1 = \frac{\Delta(C_2V)}{W}\,\frac{(x + y)}{2y} \qquad (3)$$

Here C_1 and C_2 are expressed in moles per milliliter.

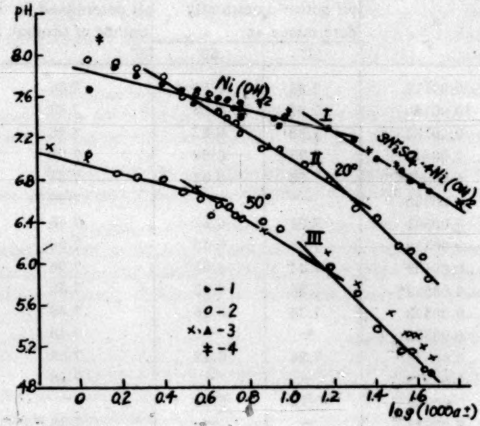

Fig. 1. Relation of the pH of initial solid phase formation vs. the logarithm of nickel sulfate activity in solution.

1) Our data at 20°, obtained by the Gromov method; 2) our data, obtained from the potentiometric titration curves at 20° and 50°; 3) data of Rotinyan and Zeldes at 50° [4] and at 20° [11]; 4) data of Akselrud and Fialkov [3].

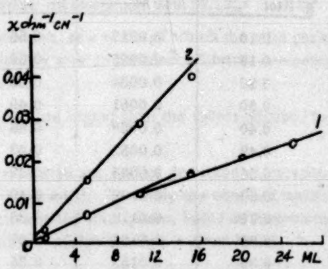

Fig. 2. Change in the specific conductance of nickel and sodium sulfate solutions with change in concentration.

1) Relation between the specific conductance of nickel sulfate solution and salt concentration, expressed in milliliters of 0.681 M $NiSO_4$ solution in 50 ml of solution, 2) Analogous curve for sodium sulfate; initial concentration of $NaSO_4$ solution 1 M.

When the above indicated conditions are observed in the experiment the change in the specific conductances of nickel and sodium sulfates will be:

$$\Delta \kappa_{NiSO_4} = -K_1 \Delta C_1 = -K_1 \frac{\Delta(C_2V)}{W} \frac{(x+y)}{2y}; \quad (4)$$

$$\Delta \kappa_{Na_2SO_4} = K_2 \frac{\Delta(C_2V)}{2W}. \quad (5)$$

Consequently, the total change in conductivity will be determined by the expression

$$\Delta \kappa_{\Sigma} = \frac{\Delta(C_2V)}{2W} \left[K_2 - K_1 \frac{(x+y)}{y} \right], \quad (6)$$

from which it is seen that the change in the specific conductance of the solution during precipitation of the basic salts or hydroxides should as a first approximation be proportional to the amount of added alkali. In other words, the relation $\kappa_{\Sigma} - C_2V$ should be expressed by a straight line in the whole concentration interval for the original salt in which a precipitate of constant composition is obtained.

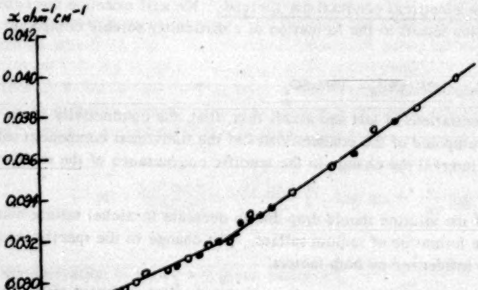

Fig. 3. Change in the specific conductance of the solution during the precipitation of nickel from sulfate solution with alkali.

With changes in the composition of the precipitate the indicated straight line will suffer breaks.

The tangent to the slope of each straight portion is equal to

$$\frac{\Delta\kappa_{\Sigma}}{\Delta(C_2V)/2W} = K_2 - K_1\,\frac{(x+y)}{y}. \qquad (7)$$

Equation (7) makes if possible to determine the composition of the precipitate (values x and y) from the slope of the linear function $\kappa_{\Sigma}, -C_2V$, provided constants K_1 and K_2 are known.

The latter are determined from the individual conductivity measurements of pure nickel sulfate and sodium sulfate solutions at different concentrations. 0.681 M Nickel sulfate solution and 1.000 M sodium sulfate solution were used to determine the constants K_1 and K_2. Both salts were carefully purified beforehand.

The different amounts of salt solution were made up to 50 ml with distilled water, after which the electrical conductivity of the solution was determined with the aid of the ordinary bridge scheme. The determination results are given in Fig.2, from which it can be seen that under experimental conditions the change in specific conductance with change in concentration is indeed linear.

Inasmuch as constants K_1 and K_2 denote the change in the specific conductance of $NiSO_4$ and Na_2SO_4 solutions with unit change in concentration, then evidently

$$K_1 = \frac{\Delta\kappa_{NiSO_4}}{\Delta C_{NiSO_4}} \text{ and } K_2 = \frac{\Delta\kappa_{Na_2SO_4}}{\Delta C_{Na_2SO_4}} \qquad (8)$$

We started with a solution of nickel sulfate in our experiments. Consequently, for calculating K_1 in the initial experimental stages it is necessary to take the slope coefficient of the straight line corresponding to the higher concentrations of nickel sulfate, while for calculating K_2 it is necessary to use the values corresponding to low concentrations of sodium sulfate.

The calculation of constants K_1 and K_2 under these conditions gives:

$$K_1 = \frac{8.3\cdot 10^{-4}\cdot 50\cdot 1000}{0.681} = 61.8$$

$$K_2 = \frac{26.5\cdot 10^{-4}\cdot 50\cdot 1000}{1} = 132.5.$$

At low concentrations of nickel sulfate

$$K_1 = \frac{11.5\cdot 10^{-4}\cdot 50\cdot 1000}{0.681} = 84.4$$

A number of solutions were prepared for the nickel precipitation experiments, the solutions containing 25 ml of 1 M $NiSO_4$ and various amounts of 1.75 M NaOH; after this the solutions were made up to 50 ml. The solutions were filtered and the specific conductances were determined at 20°, either on the following day or immediately. The results of two parallel experiments, in which the solutions were filtered and the specific conductances determined on the second day after precipitation of the nickel with alkali, are given in Fig. 3. The starting solution was acidified slightly, as a result of which the first portions of alkali were consumedin neutralizing the excess acidity and the specific conductance dropped. From Fig. 3 it can be seen that the obtained data arrange themselves along two linear sections.

The slope coefficient corresponding to the higher concentrations of nickel sulfate is

$$\frac{4.4\cdot 10^{-4}\cdot 10\cdot 1000}{1.75} = 25.1,$$

while for more dilute solutions it is

$$\frac{7.1\cdot 10^{-4}\cdot 10\cdot 1000}{1.75} = 40.5$$

The values x and y are determined from these slope coefficient values and the constants K_1 and K_2.

For the first section x = 0.74 y, while for the second,* $\frac{x+y}{y} = 1.09$, i.e., as an approximation x = 0 and y = 1.

In calculating the composition of the solid phase in this case $K_1 = 84.4$ and $K_2 = 132.5$. The last constant was used on the assumption that it is valid up to fairly high concentrations of sodium sulfate.

As a result, from the conductivity measurements it follows that the precipitate corresponding to the first section of the curve in Fig. 3 has the composition $3NiSO_4 \cdot 4Ni(OH)_2$, while the second section corresponds to $Ni(OH)_2$.

The experiments in which the precipitate was not allowed to stand with the solution gave analogous results, and consequently are not presented here.

The developed method has the advantage that it permits determining the composition of the precipitated compound, even if the latter is not found in equilibrium with the solution, whereas the determination method based on the slope of the linear function $pH - \log a_{\pm}$ assumes that the solid phase is in equilibrium with the solution.

DISCUSSION OF RESULTS

First of all it should be mentioned that the slope coefficient and electrical conductivity methods are in excellent agreement as regards the composition values obtained for the solid phase. Both the calculations according to Equation (1) and the conductivity method lead to the conclusion that in dilute solutions pure nickelous hydroxide is formed, whereas in more concentrated solutions the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ is precipitated.

Basic conclusions may be derived from a comparison of the results obtained by the "equilibrium" method of Gromov and the "rapid" potentiometric titration method. If the data obtained with these methods agree with each other at low concentrations of nickel sulfate, then significant and regular differences exist in more concentrated solutions.

The conductivity method shows that in the case of rapid titration the composition of the precipitate is such that it is in equilibrium with a more concentrated nickel sulfate solution.

This circumstance makes it possible to interpret the data of the potentiometric titration method.

Specifically, from Fig. 1 it follows that at low salt concentrations the pure nickelous hydroxide is formed, and then, insofar as the solid phase in all cases is in equilibrium with the solution, the pH values obtained from the potentiometric titration curves and by the Gromov method coincide with each other. In more concentrated nickel sulfate solutions the basic salt is formed during titration, which only after a long period of time is transformed into pure nickelous hydroxide (cf. left section of Curve II).

The composition of the pseudoequilibrium compound under the given conditions corresponds to $3NiSO_4 \cdot 4Ni(OH)_2$, i.e., it corresponds to the composition of the basic salt found in equilibrium with the solution in the region of higher nickels sulfate activities. It should be mentioned that the slope coefficient for this section of Curve II (Fig. 1) is equal to the slope coefficient of the extreme right section of equilibrium Curve I.

At even higher nickel sulfate concentrations the first precipitated basic salt has a less basic character than before, which with the passage of time is transformed not into the pure hydroxide but instead into a more basic salt, namely $3NiSO_4 \cdot 4Ni(OH)_2$.

If the composition of the second pseudoequilibrium salt is calculated from the slope coefficient of Curve II (right section), then it corresponds to the formula $3NiSO_4 \cdot 2Ni(OH)_2$.

Under equilibrium conditions this salt is probably formed at extremely high nickel sulfate activities, which activities were not attained in our experiments; consequently, on the equilibrium Curve I the section with the same slope coefficient is not shown.

Curve III (Fig. 1), obtained by the potentiometric method at 50°, shows that the slope coefficients remain constant when the temperature is raised. This condition serves as evidence that the same difficultly soluble compounds are formed at 50° and at room temperature.

It should also be mentioned that our data are in satisfactory agreement with the earlier obained values [4].

On the basis of the obtained data, it may be concluded that in general the potentiometric titration method, as well as the other "rapid" methods for determining the pH at the beginning of solid phase formation, do not give the right to calculate the free energy of formation of the salt.

In conclusion, we wish to state that the possibility of forming pseudoequilibrium compounds limits even more the practical use of the so-called pH series for the precipitation of hydroxides [1,2], for the solution of concrete problems is governed, not by the equilibrium pH values existing at the beginning of solid phase formation, but by those pH values that are established under the given process rate.

Calculation of the standard isobaric potentials on the basis of the equilibrium curve leads to the following values.

The standard isobaric potential for the formation of nickelous hydroxide from the ions is −20.8 kcal/ mole, whereas the value −18.9 kcal/ mole was obtained earlier.

The standard isobaric potential for the formation of the basic salt $3NiSO_4 \cdot 4Ni(OH)_2 (\Delta Z^0_{basic})$ is −96.0 kcal for 1 mole of basic salt and the standard isobaric potential for the addition of 3 moles of nickel sulfate to 4 moles of nickelous hydroxide ($\Delta Z^0_{addn.}$) is −20.4 kcal for 1 mole of basic salt.

SUMMARY

1. The method of analyzing the equilibrium curves $pH - \log a_{\pm}$ was used to determine the compositions of difficultly soluble nickel salts formed in the treatment of $NiSO_4$ solutions with alkali solutions.

2. The obtained results were verified by the method of analyzing the conductivity curves for the mother liquors during the precipitation of basic nickel salts with alkali.

3. It was shown that at low nickel sulfate activities the pure hydroxide is formed, while at higher activities the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ is formed. The standard isobaric potentials for the formation of these compounds were calculated, as was also the standard isobaric potential for the addition of nickel sulfate to nickelous hydroxide with the formation of $3NiSO_4 \cdot 4Ni(OH)_2$.

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The standard isobaric potential for the formation of [illegible]

SUMMARY

1. The method of [illegible]

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BINARY SYSTEM RUBIDIUM SULFATE-MAGNESIUM SULFATE

V. E. Plyushchev and N. F. Markovskaya

Insofar as we know, the binary system of rubidium and magnesium sulfates has not been studied.

Only the formation of the binary sulfates of rubidium and magnesium, $Rb_2SO_4 \cdot MgSO_4$ and $Rb_2SO_4 \cdot 2MgSO_4$ is indicated in the literature. According to the data of Mallet [1,2], both compounds can be obtained by cooling a melt of the anhydrous components taken in the proper proportions. The compound $Rb_2SO_4 \cdot 2MgSO_4$ is an analog of langbeinite and possesses identical properties.

EXPERIMENTAL

In our work the system $Rb_2SO_4-MgSO_4$ was studied by the melting point method, a pyrometer of the Kurnakov type being used to record the cooling (heating) curves. The Pt-PtRh thermocouple was mounted in combination and was calibrated from the transition and melting points of chemically pure $Na_2SO_4 \cdot 10\ H_2O$, Na_2SO_4, K_2SO_4, and also from the melting points of $K_2Cr_2O_7$, NaCl, and eutectic in the system Na_2SO_4-NaCl.

As a rule, the melts were prepared with 5% increment changes in the composition; some sections of the fusion diagram, as can be seen from the table, were studied in greater detail. The starting salts used in studying the system were chemically pure Rb_2SO_4 and $MgSO_4 \cdot 7H_2O$, anhydrous magnesium sulfate being obtained from the latter. The purity of these sulfates was verified by spectral analysis.

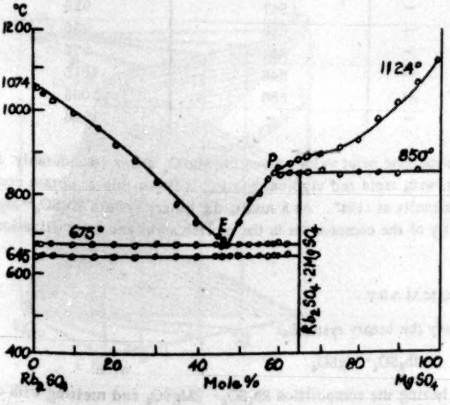

Fig. Melting-point diagram of the system rubidium sulfate - magnesium sulfate

The presence of a eutectic point in the melts with a high $RbSO_4$ content leads to the conclusion that solid solutions are not formed on a rubidium sulfate base, at least not in the region of investigated concentrations. Also, solid solutions were not revealed in the region of high magnesium sulfate concentrations.

The system has two characteristic points – the transition point (P) and the eutectic (E). The first, corresponding to 59 mole % $MgSO_4$, reflects the existence in the system of the compound melting with decomposition at 850°. The maximum duration of the halts at 850° is observed in the case of the melt containing 66.7 mole % $MgSO_4$. This circumstance permits assigning to the compound the formula $Rb_2SO_4 \cdot 2MgSO_4$. The existence of the compound is confirmed by the character of the thermal diagram for the melts and by X-ray phase analysis.

No other compounds are present in the system. The eutectic, formed from α-Rb_2SO_4 and compound, corresponds to 675° and 47.5 mole % $MgSO_4$.

The cooling (heating) curves of the melt containing 47.5 mole % $MgSO_4$, having only two temperature halts responding to the eutectic line and the conversion of α-Rb_2SO_4 into β-Rb_2SO_4, demonstrate the presence of a eutectic.

The derived conclusions on the character of the system are confirmed by the microstructure of the melts.

TABLE

$MgSO_4$ (in mole %)	Temperature			
	Polymorphic transformation of Rb_2SO_4	Eutectic	Formation of compound $Rb_2SO_4 \cdot 2MgSO_4$	Melting point
0.0	645°	–	–	1074°
1.0	645	676°	–	1058
2.5	646	675	–	1040
5.0	643	677	–	1026
10.0	645	672	–	995
15.0	645	675	–	955
20.0	648	675	–	918
25.0	645	672	–	882
30.0	645	678	–	830
35.0	648	675	–	775
40.0	645	675	–	728
45.0	645	673	–	700
46.5	645	675	–	685
47.5	645	675	–	675
50.0	648	675	–	728
52.5	648	675	–	785
55.0	642	675	–	800
57.5	645	678	–	830
59.0	645	675	850°	850
60.0	645	675	850	860
62.5	645	675	850	870
65.0	–	–	850	880
66.7	–	–	850	890
70.0	–	–	853	898
75.0	–	–	847	910
80.0	–	–	850	930
85.0	–	–	848	975
90.0	–	–	846	1015
95.0	–	–	850	1065
100.0	–	–	–	1124

It should be mentioned that in the literature the melting point values given for $MgSO_4$ differ considerably, due to decomposition of the latter during fusion. However, with rapid and vigorous heating it is possible to obtain concordant results. According to our data magnesium sulfate melts at 1124°. As a result, the binary system $Rb_2SO_4-MgSO_4$ belongs to the type of system with unlimited miscibility of the components in the molten state and crystallization of a chemical compound melting with decomposition.

SUMMARY

1. The thermal analysis method was used to study the binary system

$Rb_2SO_4-MgSO_4$.

2. The existence in the system of a compound having the composition $Rb_2SO_4 \cdot 2MgSO_4$ and melting with decomposition was established.

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DOUBLE DECOMPOSITION IN THE ABSENCE OF SOLVENT

I. QUATERNARY RECIPROCAL SYSTEM OF LITHIUM AND POTASSIUM CHLORIDES, SULFATES AND TUNGSTATES

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

The study of metallic tungstates in melts attracts the natural and deserved interest of investigators. We studied a number of ternary reciprocal systems in which lithium and potassium tungstates were present [1]. An even more interesting problem is the behavior of these tungstates in the make-up of a complex multicomponent system - the quaternary reciprocal system Li, K || Cl, SO_4, WO_4. The visual-polythermal method [2] was used to study the given system.

EXPERIMENTAL

The system studied by us, in the form of a triangular prism [3] (Fig. 1), has at the apexes the components with the following melting points Li_2Cl_2 606°, Li_2SO_4 860°, Li_2WO_4 738°, K_2Cl_2 774°, K_2SO_4 1069°, K_2WO_4 926°. Lithium chloride differed from the other salts in being extremely hydroscopic, which required constant drying of the salt and determination of its weight by difference from the box. Nearly all of the components are characterized by transformation points at different temperatures. Thus, it was established: for lithium chloride homeomorphic transformation at 565° [4], for potassium chloride at 27 and 384° [5], for lithium sulfate heteromorphic transformation at 572° [6], for lithium tungstate heteromorphic transformation at 660° [7].

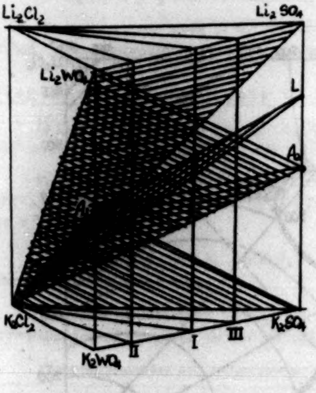

Fig. 1. Section scheme through the quaternary reciprocal system Li, K || Cl, SO_4, WO_4.

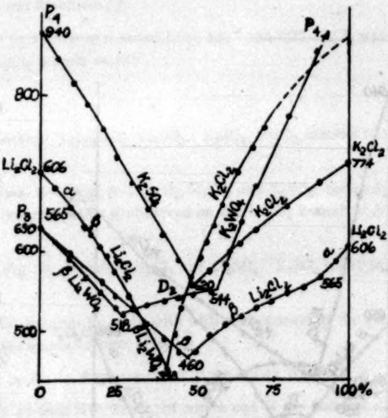

Fig. 2. Sides of book section I.

The results of our studies on the base of the prism — the ternary systems K || Cl, SO_4, WO_4 and Li || Cl, SO_4, WO_4, and also of the sides of the prism — the ternary reciprocal systems Li, K || Cl, WO_4 and Li, K || SO_4, WO_4* — are being published in separate papers.

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* The third side of the given prism — the ternary reciprocal system Li, K || Cl, SO_4 — was studied by Dombrovskaya [8] and later by Bergman and Akopov. We used the data of the latter authors.

For the complete study of the internal structure of this prism there were taken three book and five internal triangular sections through the composition prism(Fig. 1).

The results of studying the book sections are briefly described below.

Book Sections of the Quaternary Reciprocal System Li, K ‖ Cl, SO_4, WO_4

The book sections were conditionally taken and studied as ternary reciprocal systems depicted in the form of rectangles. The following sections are to be found in the composition prism.

TABLE 1

Binary Systems

P_3-P_4*		$P_3-Li_2Cl_2$		$P_4-K_2Cl_2$		$Li_2Cl_2-K_2Cl_2$	
% P_4	Temperature	% P_3	Temperature	% K_2Cl_2	Temperature	% K_2Cl_2	Temperature
0	630°	0	606°	0	940°	0	606°
10	590	10	565	10	878	10	560
20	544	20	542	20	816	20	510
25	525	30	526	30	750	30	448
27.5	518	40	504	40	685	40	368
30	524	45	490	45	650	45	462
40	535	50	468	50	620	50	472
50	512	52.5	460	55	636	55	516
55	544	55	468	60	650	60	564
57.5	544	60	485	70	688	65	604
60	578	70	524	80	718	70	638
70	680	80	558	90	750	75	664
80	772	100	630	100	774	80	690

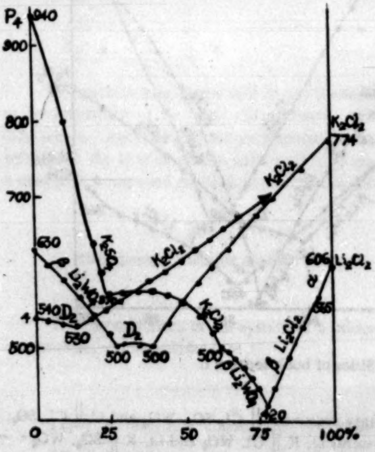

Fig. 3. Curves of Section I.

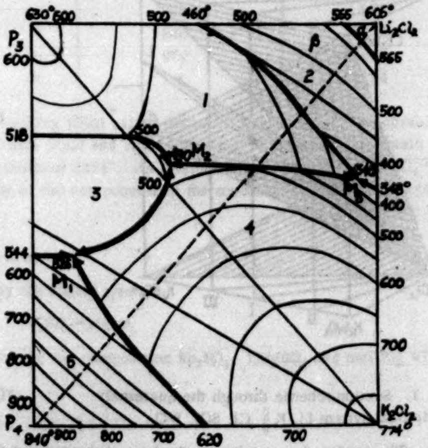
630°
600
500
460°
500
555
605°
Li₂Cl₂
P₃
600
565
β
2
1
500
518
500
480
M₂
400
348°
500
3
400
4
500
544
600
PT₁
600
700
700
800
6
900
P₄
K₂Cl₂
840°
900
800
700
620
700
774°

Fig. 4. Section I. 1) β -Li_2WO_4, 2) Li_2Cl_2, 3) $Li_2SO_4 \cdot K_2SO_4$, 4) K_2Cl_2, 5) K_2SO_4.

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* We will conditionally designate: (50% Li_2WO_4 + 50% Li_2SO_4) by P_3, and (50% K_2WO_4 + 50% K_2SO_4) by P_4.

TABLE 2

Diagonal				Internal Section (50 % P_3 50% P_4)$-K_2Cl_2$	
$P_3-K_2Cl_2$		$P_4-Li_2Cl_2$			
% K_2Cl_2	Temperature	% P_4	Temperature	% K_2Cl_2	Temperature
0	630°	0	606°	0	540°
10	590	10	528	5	537
20	544	20	445	10	535
25	518	22.5	420	15	530
27.5	500	25	445	20	540
30	503	35	495	25	552
35	503	37.5	500	30	565
40	500	40	520	35	580
45	530	50	560	40	592
50	560	60	572	45	605
60	605	70	574	50	620
70	650	77.5	600	60	645
80	696	80	640	70	678

Book section I (50% Li_2WO_4 + 50% Li_2SO_4)$-$(50% K_2WO + 50% K_2SO_4)$-Li_2Cl_2-K_2Cl_2$.

The sides of the rectangle are the sections (Table 1, Fig. 2): *

1) (50% Li_2WO_4 + 50% Li_2SO_4)$-$(50% K_2WO_4 + 50% K_2SO_4)** $-$ branches β-Li_2WO_4, $Li_2SO_4 \cdot K_2SO_4$,*** P_4 intersect at 518° and 27.5% P_4, 544° and 57.7% P_4.

2) (50% Li_2WO_4 + 50% Li_2SO_4)$-Li_2Cl_2$ $-$ branches Li_2Cl_2 and P_3 intersect at 460° and 52.5% P_3. Branch Li_2Cl_2 is complicated by homeomorphic transformation at 565° and 10% P_3.

3) (50% K_2WO_4 + 50% K_2SO_4)$-K_2Cl_2$ $-$ branches P_4 and K_2Cl_2 intersect at 620° and 50% K_2Cl_2.

4) $Li_2Cl_2-K_2Cl_2$ was first studied by Zhemchuzhnyi and Rambakh [9].

We repeated our study of the system liquidus and the existence of a eutectic at 348° and 42% K_2Cl_2 was established. Homeomorphic transformation was noted on the Li_2Cl_2 branch at 565°.

Diagonal Sections (Table 2, Figure 3)

1) (50% Li_2WO_4 + 50% Li_2SO_4)$-K_2Cl_2$ have three branches: β-Li_2WO_4, $Li_2SO_4 \cdot K_2SO_4$, K_2Cl_2, intersecting at 500° and 27.5 % K_2Cl_2, 500° and 40% K_2Cl_2.

2) (50% K_2WO_4 + 50% K_2SO_4)$-Li_2Cl_2$ has four branches: β-Li_2Cl_2, β-Li_2WO_4, K_2Cl_2 and K_2SO_4, intersecting at 420° and 22.5% P_4, 500° and 37.5% P_4, 570° and 76% P_4. Polymorphism is observed on the Li_2Cl_2 branch at 565° and 5% P_4.

Internal section (50% P_3 + 50% P_4)$-K_2Cl_2$ (Table 2, Fig. 3), branches K_2Cl_2 and $Li_2SO_4 \cdot K_2SO_4$ meet in the transition point at 530° and 15% K_2Cl_2.

A number of cuts **** through the rectangle made it possible to study with sufficient accuracy the surface of crystallization of the given section through the quaternary reciprocal system (Fig. 4).

The compositions and temperatures of the univariant points in the system are given below in Table 3.

The surface of crystallization of the section is broken up into five fields, of which one is the field of the binary compound 1:1 $Li_2SO_4 \cdot K_2SO_4$, while the remaining are fields of the components.

The calculated areas of the crystallization fields, expressed in area per cent of the rectangle, are: α-$Li_2Cl_2$$-$0.6, β-$Li_2Cl_2$$-$9.6, β-$Li_2WO_4$$-$23.4, $K_2SO_4$$-$12.3, $K_2Cl_2$$-$43.42, $Li_2SO_4 \cdot K_2SO_4$$-$10.68%.

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* Only the more important points are indicated in the tables. All of the points are given in the figures.

** We will conditionally designate: (50% Li_2WO_4 + 50% Li_2SO_4) by P_3, and (50% K_2WO_4 + 50% K_2SO_4) by P_4.

*** We will designate the compound $Li_2SO_4 \cdot K_2SO_4$ by D_2.

**** In all three book sections 10 cuts per section were made through the surface of crystallization. Due to the voluminous nature of the material the curves and tables of all of these cuts are not given in this paper.

TABLE 3

Point	Temperature	Composition (in mole %)				Equilibrium phases
		K_2Cl_2	P_3	P_4	Li_2Cl_2	
M_1	526°	10	42	48	–	K_2SO_4, D_2, K_2Cl_2.
M_2	490	–	24	35	41	Li_2WO_4, D_2, K_2Cl_2.
M_3	340	38.4	6	–	55.5	Li_2WO_4, K_2Cl_2, Li_2Cl_2.

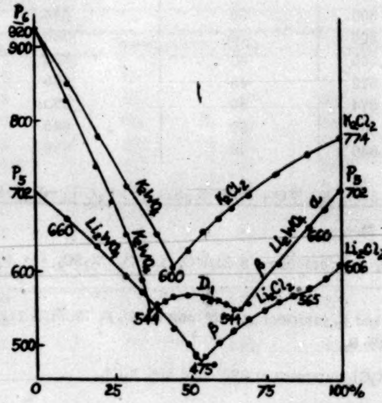

Fig. 5. Sides of Book Section II.

As a result, the given section establishes the fact that the complex compound $Li_2SO_4 \cdot K_2SO_4$, melting without decomposition, retains its stability also inside the system. Characteristic are the planar form of the complex and almost the complete absence of isotherms.

Complex formation is the predominant reaction in the system.

Book Section II (80% Li_2WO_4 + 20% Li_2SO_4) − (80% K_2WO_4 + 20% K_2SO_4)− Li_2Cl_2−K_2Cl_2.

The rectangle is composed of the following sections (Table 4, Fig. 5):

1) (80% Li_2WO_4 + 20% Li_2SO_4)−(80% K_2WO_4 + 20% K_2SO_4)* branches: Li_2WO_4, compound $Li_2WO_4 \cdot K_2WO_4$** intersect at 544° and 33% P_6, 544° and 62.5% P_6. Branch Li_2WO_4 at 660° and 10% P_6 is complicated by polymorphic transformation.

2) (80% Li_2WO_4 + 20% Li_2SO_4)−Li_2Cl_2− branches P_5 and Li_2Cl_2 intersect at 475° and 46.5% P_5. Homeomorphic transformation is observed on branch Li_2Cl_2 at 565° and 15% P_5. Branch Li_2WO_4 separates into the α - and β -modifications at 660° and 87.5 %. P_5.

3) (80% K_2WO_4 + 20% K_2SO_4)−K_2Cl_2− branches K_2Cl_2 and K_2WO_4 intersect at 600° and 45% K_2Cl_2.

4) Li_2Cl_2−K_2Cl_2−eutectic at 358° and 42% K_2Cl_2 (Table 1, Fig. 2).

TABLE 4
Binary System

P_5-P_6		$P_6-K_2Cl_2$		$P_5-Li_2Cl_2$	
% P_6	Temperature	% K_2Cl_2	Temperature	% P_5	Temperature
0	702°	0	920°	0	606°
10	660	10	846	10	575
20	606	20	774	15	564
30	550	30	710	20	566
32.5	546	40	646	30	532
35	546	45	600	40	500
40	556	50	624	45	482
45	560	55	648	47.5	482
50	565	60	665	50	500
55	562	65	680	55	520
60	552	70	698	60	544
62.5	544	80	725	70	590
65	584	90	750	80	628
75	690	100	774	90	665

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* For convenience we will designate the composition (80% Li_2WO_4 + 20% Li_2SO_4) by P_5, (80% K_2WO_4 + 20% K_2SO_4) by P_6.

** For convenience we will designate the compound 1 : 1 $Li_2WO_4 \cdot K_2WO_4$ by D_1.

Diagonal Sections (Table 5, Figure 6)

1) P$_5$—K$_2$Cl$_2$— intersection of branches P$_5$ and K$_2$Cl$_2$ at 522° and 42% K$_2$Cl$_2$. Polymorphism of Li$_2$WO$_4$ was observed at 660° and 6.5% K$_2$Cl$_2$.

2) P$_6$—Li$_2$Cl$_2$— branches Li$_2$Cl$_2$, β-Li$_2$WO$_4$, K$_2$Cl$_2$, K$_2$WO$_4$ intersect at 438° and 20% P$_6$; 545° and 45% P$_6$; 545° and 78% P$_6$.

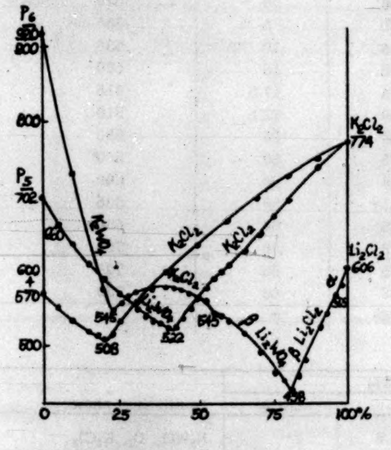


Fig. 6. Curves of Section II.

Polymorphism was observed on branch Li$_2$Cl$_2$ at 565° and 5% P$_6$. Internal section (50% P$_5$ + 50% P$_6$)—K$_2$Cl$_2$ (Table 5, Fig. 6), two branches intersect at 508° and 21% K$_2$Cl$_2$.

A study of a number of sections through the given rectangle made it possible to depict with the necessary accuracy the surface of crystallization of this book section through the quaternary composite system (Fig. 7). It consists of five fields, representing in per cent to the total area of the rectangle: K$_2$Cl$_2$—40.1, K$_2$WO$_4$—9.9, field of the compound 1 : 1 Li$_2$WO$_4$ · K$_2$WO$_4$—9.9, α - and β -LiWO$_4$ —31, α - and β -Li$_2$Cl$_2$— 9.1%.

The crystallization fields converge into three univariant points, the compositions and temperatures of which are given in Table 6.

The field of compound 1 : 1 Li$_2$WO$_4$ · K$_2$WO$_4$ has a planar form and is characterized by the absence of isotherms. Being a compound that melts without decomposition, it retains its stability inside the section and quite deeply dislodges the fields of the components.

The lithium tungstate field, having an elongated form, separates into α - and β -portions. The isotherms of the potassium chloride field are characterized by a convex shape, becoming somewhat flatter when the temperature is lowered. In the lithium chloride field sections of homeomorphic transformations were also observed. Finally, the potassium tungstate field is characterized by steep slope isotherms with frequent decomposition. Complex formation is the predominant reaction in the system.

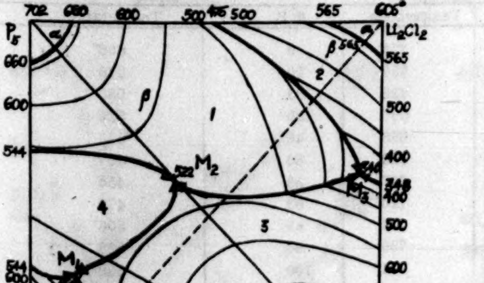


Fig. 7. Section II.

1) Li$_2$WO$_4$, 2) LiCl$_2$, 3) K$_2$Cl$_2$, 4) Li$_2$WO$_4$ · K$_2$WO$_4$, 5) K$_2$WO$_4$.

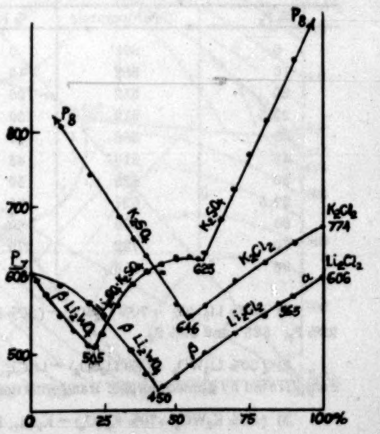


Fig. 8. Sides of Book Section III.

Book Section III $(30\%\ Li_2WO_4 + 70\%\ Li_2SO_4)-(30\%\ K_2WO_4 + 70\%\ K_2SO_4)-Li_2Cl_2-K_2Cl_2$.

The following sections compose the rectangle of the given book section (Table 7, Fig. 8):

TABLE 5

Diagonal				Section	
$P_5-K_2Cl_2$		$P_6-Li_2Cl_2$		$(50\%\ P_5 + 50\%\ P_6)-K_2Cl_2$	
% K_2Cl_2	Temperature	% P_6	Temperature	% K_2Cl_2	Temperature
0	702°	0	606°	0	570°
10	638	2.5	580	5	550
20	590	5	565	10	535
30	550	7.5	545	15	520
35	535	10	525	17.5	515
37.5	530	17.5	460	22.5	516
40	525	20	438	25	530
42.5	525	25	465	30	560
45	538	35	518	40	600
47.5	550	45	545	50	635
50	565	50	565	60	666
70	648	60	578	70	700
80	698	70	575	80	728
90	740	77.5	548	90	750
–	–	80	576	–	–

TABLE 6

Point	Temperature	Composition (in mole%)				Equilibrium phases
		K_2Cl_2	P_5	P_6	Li_2Cl_2	
M_1	496°	11.5	37	51.5	–	K_2WO_4, D_1, K_2Cl_2.
M_2	522	41.5	58.5	–	–	D_1, Li_2WO_4, K_2Cl_2.
M_3	340	40	7.5	–	52.5	Li_2WO_4, Li_2Cl_2, K_2Cl_2.

TABLE 7
Binary System

P_7-P_8		$P_8-K_2Cl_2$		$P_7-Li_2Cl_2$	
% P_8	Temperature	% P_8	Temperature	% P_7	Temperature
0	608°	0	774°	0	606°
10	552	10	750	10	576
20	512	20	726	20	550
22.5	512	30	697	30	525
30	566	40	665	40	500
40	610	45	650	50	467
50	625	50	667	55	455
57.5	627	55	710	60	472
60	635	60	732	65	506
70	722	70	786	80	568
80	816	80	844	100	608

1) $(30\%\ Li_2WO_4 + 70\%\ Li_2SO_4)-(30\%\ K_2WO_4\ 70\%\ K_2SO_4)$• branches β-Li_2WO_4, D_2, K_2SO_4 intersect at 505° and 22% P_8; 625° and 59% P_8.

2) $(30\%\ Li_2WO_4 + 70\%\ Li_2SO_4)-Li_2Cl_2$, branches P_7 and Li_2Cl_2 intersect at 450° and 56.5% P_7. Branch Li_2Cl_2 is complicated by homeomorphic transformation at 565° and 85% Li_2Cl_2.

3) $(30\%\ K_2WO_4 + 70\%\ K_2SO_4)-K_2Cl_2$, branches P_8 and K_2Cl_2 intersect at 646° and 46.5% P_8.

4) $Li_2Cl_2-K_2Cl_2$ – eutectic at 348° and 42% K_2Cl_2.

• For convenience we will designate the composition $(30\%\ Li_2WO_4 + 70\%\ Li_2SO_4)$ by P_7 and the composition $(30\%\ K_2WO_4 + 70\%\ K_2SO_4)$ by P_8.

Diagonal Sections (Table 8, Figure 9)

1) $P_8-Li_2Cl_2$, – 2) branches Li_2Cl_2, β-Li_2WO_4, K_2Cl_2, K_2SO_4 intersect at 403° and 21.5 % P_8, 470° and 35% P_8, 580° and 75% P_8. On branch Li_2Cl_2 homeomorphism was observed at 565° and 5% P_8. $P_7-K_2Cl_2$ – intersection of branches Li_2WO_4, K_2Cl_2 and D_2 at 475° and 27.5% K_2Cl_2; 475° and 32% K_2Cl_2.

Internal section: (50% P_8 + 50% P_7)$-K_2Cl_2$ (Table 8, Fig. 9).

TABLE 8

Diagonal				Section	
$P_8-Li_2Cl_2$		$P_7-K_2Cl_2$		50% P_8 + 50% P_7 $-K_2Cl_2$	
% P_8	Temperature	% K_2Cl_2	Temperature	% K_2Cl_2	Temperature
0	606°	0	608°	0	625°
5	565	10	544	10	578
15	472	20	500	15	557
20	418	25	485	17.5	548
30	450	27.5	475	20	542
35	470	30	478	22.5	548
40	518	32.5	480	25	555
50	576	37.5	475	30	565
60	585	40	500	40	590
70	585	50	576	50	614
75	580	60	612	60	640
80	660	70	656	70	668
–	–	80	696	–	–

TABLE 9

Point	Temperature	Composition (in mole%)				Equilibrium phases
		K_2Cl_2	P_7	P_8	Li_2Cl_2	
M_1	535°	15	40	45	–	K_2SO_4, D_2, K_2Cl_2.
M_2	460	–	32.5	32.5	35	Li_2WO_4, D_2, K_2Cl_2.
M_3	336	36.5	3.5	–	60	Li_2Cl_2, Li_2WO_4, K_2Cl_2.

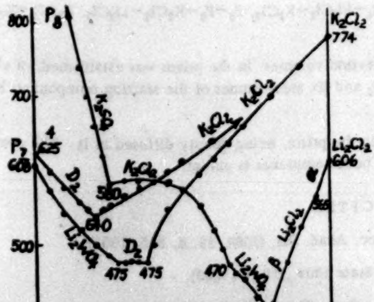
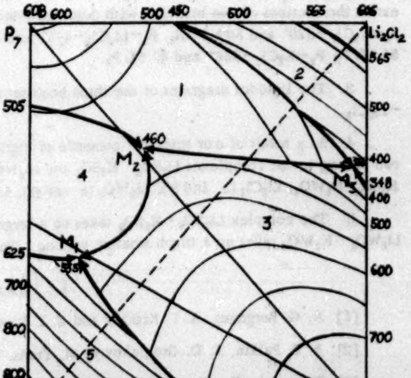


Fig. 9. Curves of Section III.



608
600
500
450
500
565
606
P_7
Li_2Cl_2
565
1
2
505
500
460
M_2
4
400
M_3
348
400
3
500
625
M_1
535
600
700
800
5
700
800
P_8
880
800
800
700
646
700
K_2Cl_2
774

Fig. 10. Section III.

1) Li_2WO_4, 2) Li_2Cl_2, 3) K_2Cl_2, 4) $Li_2SO_4 \cdot K_2SO_4$, 5) K_2SO_4.

The branches of compounds $Li_2SO_4 \cdot K_2SO_4$ and K_2Cl_2 intersect at 540° and 19% K_2Cl_2.

As the result of studying the surface of crystallization of the given book section (Fig. 10) with the aid of ten cuts it was established that the five crystallization fields of the section converge into three univariant points. We present their compositions and temperatures in Table 9.

The areas of the crystallization fields in per cent of the total area of the rectangle are: $K_2SO_4-12.70$, field of compound $Li_2SO_4 \cdot K_2SO_4-11.20$, $K_2Cl_2-44.28$, $Li_2WO_4-21.80$, α - and β -$Li_2Cl_2-10.02$.

Characteristic for the field of compound $Li_2SO_4 \cdot K_2SO_4$ are its planar form and the absence of isotherms.

Melting without decomposition, the field retains its stability and takes up a large volume in the total volume of the prism, driving out to a considerable degree the fields of the components. The character of the isotherms in the fields of the starting components remains the same as in the previous book sections. The reaction of the system is toward complex formation.

The Three Book Sections of the Quaternary Reciprocal System Li, K $\|$ Cl, SO_4, WO_4

It can be concluded, based on analysis of the data obtained as the results of their composition prism sectioning, that the presenee of eight crystallization volumes in the prism is supported by the three book sections, and their boundaries established.* The complex $Li_2SO_4 \cdot K_2SO_4$, obtained in the ternary reciprocal system Li, K $\|$ Cl, SO_4, appearing as the outer boundar y of the composition prism, is also confirmed inside the prism by book sections I and III.

In all three sections the reaction of complex formation predominates over the decomposition reactions.

As a result, the compound $Li_2SO_4 \cdot K_2SO_4$, melting without decomposition, retains its stability also inside the composition prism. It takes up quite a large volume in the prism, deeply penetrating into it and somewhat "oppressing" as it were the volume of the other complex $Li_2WO_4 \cdot K_2WO_4$, situated on the opposite side. This second complex, 1:1 $Li_2WO_4 \cdot K_2WO_4$, obtained in the ternary reciprocal system Li, K $\|$ Cl, WO_4, is confirmed by book section II. The reaction of complex formation in this section predominates over the decomposition reactions to a considerably lesser degree than in the previous two book sections. This is also confirmed by the much smaller volume occupied by the tungstate complex 1:1 $Li_2WO_4 \cdot K_2WO_4$, when compared with the volume of the sulfate complex 1:1 $Li_2SO_4 \cdot K_2SO_4$.

SUMMARY

1. The three book sections through the reciprocal prism system Li, K $\|$ SO_4, WO_4; were studied, namely P_3-P_4, P_5-P_6 and P_7-P_8. As a result of this study the volumes of the two complexes $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$.

2. Six sections through the upper and lower bases of the prism were studied and it was established that they appear as the sections of two branches with points of intersection at: $P_3-Li_2Cl_2$ with univariant point 460° and 52.5% P_3; $P_4-K_2Cl_2-620°$ and 50% K_2Cl_2, $P_5-Li_2Cl_2-475°$ and 46.5% P_5; $P_6-K_2Cl_2-600°$ and 45% K_2Cl_2; $P_7-Li_2Cl_2-450°$ and 56.5% P_7; $P_8-K_2Cl_2-646°$ and 46.5% P_8.

3. The liquidus diagrams of the three book sections $P_3-P_4-Li_2Cl_2-K_2Cl_2$, $P_5-P_6-K_2Cl_2-Li_2Cl_2$, $P_7-P_8-K_2Cl_2-Li_2Cl_2$.

4. As a result of our study the presence of eight crystallization volumes in the prism was established, of which two belong to the complexes $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$ and six are volumes of the starting components K_2Cl_2, K_2SO_4, K_2WO_4, Li_2Cl_2 (α and β), Li_2WO_4 (α and β), Li_2SO_4.

5. The complex $Li_2SO_4 \cdot K_2SO_4$ takes up a large volume in the prism, being deeply diffused in it. The complex $Li_2WO_4 \cdot K_2WO_4$ takes up a much smaller volume. The form of both complexes is planar.

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* The lithium sulfate field is not embraced by the book sections.

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THERMOGRAPHIC STUDY OF THE DECOMPOSITION OF BIVALENT METAL OXALATES

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There is hardly any literature data on the thermal decomposition of metal oxalates, and the available data on individual salts is incomplete and frequently contradictory. In addition, the process of dehydration (in the case of crystallohydrates) is frequently confused with the thermal decomposition of the oxalate itself.

Despite this, the decomposition of oxalates, expecially of the heavy metals, is of interest not only from the theoretical viewpoint but also from the practical side, having in mind the preparation of solid phases in chemically active form (metals, oxides, etc.).

With the aid of the thermographic method we studied the decomposition of the oxalates of Fe, Ni, Co, Mn, Cu, Zn, Cd, Hg, Sn, Pb, Mg, Ca, Sr, Ba, and also of oxalic acid. The oxalates were precipitated from the solutions of soluble metal salts (previously purified) with pure alkali oxalates (or oxalic acid) and dried at 80-100°.

In the precipitation of the oxalates care was taken not to add the alkali oxalates in amounts exceeding the theoretical so as to avoid the formation of double salts of the type $M_2C_2O_4 \cdot 3C_2O_4$, possessing entirely different solubility properties. Thus, the double oxalates of Ni and Co are difficultly soluble, while the corresponding iron derivative is readily soluble.

EXPERIMENTAL

The thermograms were made on the recording instrument of the N. S. Kurnakov system, in which programmatic thermal regulation was realized with the aid of a sensitive thermal control element and Thyratron relay, assembled according to the phase rotation scheme [1]. The potentiometric method [2] was used to calibrate the Pt-PtRh thermocouple. Al_2O_3 was used as the standard.

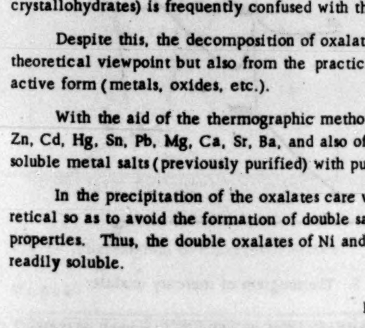

Fig. 1. Thermogram of oxalic acid, dihydrate.

According to Karyakin [3], the dihydrate of oxalic acid loses water at 98-99°, while anhydrous $H_2C_2O_4$ obtained by distillation (vacuum) melts at 189° and decomposes above this temperature into CO, CO_2, H_2O. Our thermogram for crystalline $H_2C_2O_4 \cdot 2H_2O$, obtained by the method of Kolthoff and Sandell [4], is shown in Fig. 1. As can be seen from the thermogram, water is removed at 96-99°, the acid melts at 128-153° and decomposes at 191-196°. $H_2C_2O_4$ is amorphous after removal of the water of crystallization, and consequently is characterized by a melting point range [5]. As a result, the softening of amorphous $H_2C_2O_4$, unsuccessful in attaining the crystalline state with the liberation of stored internal energy, differs from the melting of the crystalline acid $H_2C_2O_4$, obtained by distillation in vacuum (m.p. 189°').

As regards the oxalates of the bivalent metals, from the character of their thermal decomposition they can be divided into two groups. The oxalates of copper and mercury, decomposing with the evolution of heat, belong to the first group. In the thermogram for copper oxalate (Fig. 1) the weakly expressed endothermic effect denotes the removal of water, while the exothermic peaks of the ordinary and differential graphs characterize the decomposition of the anhydrous salt. In order to prove that the exotherm 320-376° relates specifically to the thermal dissociation of the oxalate, and not to the transition of CuC_2O_4 from the amorphous state (after water removal) into the crystalline state, we performed a visual experiment in the Stapanova vessel. On doing this, the pale blue CuC_2O_4 (after the endotherm) at the moment of sharp galvanometer needle deflection in the direction of heat evolution begins to rapidly turn into a dark brown mass, which is shown to be a mixture of metallic copper and its oxides.*

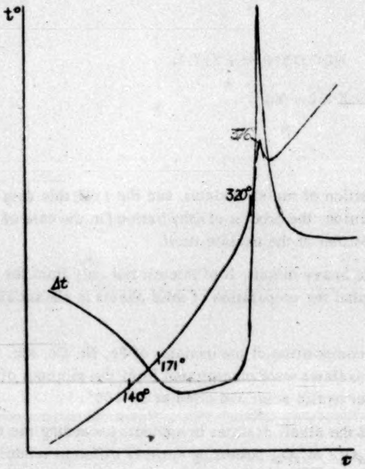

Fig. 2. Thermogram of copper oxalate

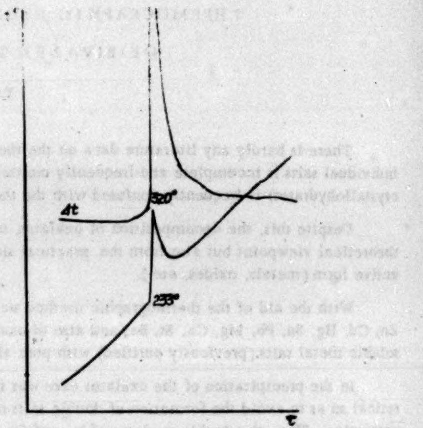

Fig. 3. Thermogram of mercury oxalate.

The endotherm is absent in the thermogram for the decomposition of HgC_2O_4 (Fig. 3) inasmuch as mercury oxalate cyrstallizes without water, while the exotherm is even more strongly expressed than in the case of copper oxalate. The specimen suffers a spontaneous rise in temperature of about 90° (exotherm 233-320°). According to Nikolaev [6], similar peaks on ordinary graphs characterize autocatalytic reactions, i.e., their rate increase is proportional to the time. Consequently, there is basis to assume that the thermal decomposition reactions for copper and mercury oxalates are autocatalytic reactions.

The oxalates of the remaining metals studied by us belong to the second group, the thermal dissociation of which is accompanied by the absorption of heat. The thermograms for $FeC_2O_4 \cdot 2H_2O$, $NiC_2O_4 \cdot 2H_2O$, $CoC_2O_4 \cdot 2H_2O$, $MnC_2O_4 \cdot 2H_2O$, $ZnC_2O_4 \cdot 2H_2O$, $MgC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ are essentially of one type and invididually possess two endothermic effects for the removal of water and decomposition of the anhydrous salt. As an example of a typical thermogram we will present the heating curve for $MnC_2O_4 \cdot 2H_2O$ (Fig. 4). Here the first endotherm 93-125° characterizes dehydration, while the second (384-412°) characterizes the decomposition of anhydrous manganese oxalate. The oxalates of the metals Co, Zn and Cd give thermograms that are of similar character but, it is understood, with different temperature values for the endothermic effects (see Table). The heating curve for $NiC_2O_4 \cdot 2H_2O$ (Fig. 5) differs somewhat from the typical thermogram in that after the removal of water, the differential graph does not return to the level of the null line (for the differential thermocouple) and the decomposition of NiC_2O_4 begins immediately, as a result of which both of the endothermic effects are not as clearly expressed as in the typical thermogram. This is explained by the greater strength of the water bond in $NiC_2O_4 \cdot 2H_2O$ (dehydration temperature is higher; see Table), after the removal of which the salt itself decomposes with comparative ease.

A peculiarity of the thermogram for $FeC_2O_4 \cdot 2H_2O$ (Fig. 6) is the presence of superheat curves [7] with respect to dehydration (214-200°). The superheat cycle shows that after the begining of dehydration (214°) the temperature drops appreciably (200°), i.e., $FeC_2O_4 \cdot 2H_2O$ is superheated by 14°. An even greater superheat cycle at the same heating rate of 12° a minute characterizes the heating curve for anhydrous PbC_2O_4 (Fig. 7), where after the beginning of salt decomposition (354°) the temperature drops to 318°. Such marked superheating (by 36°) is seen only in the case of old samples of PbC_2O_4. The curve for freshly prepared PbC_2O_4 is shown in Fig. 8**, where the superheat cycle is expressed much more weakly (by 15°) than on the curve for an old sample of PbC_2O_4 (Fig. 7). In addition, in Fig. 8 an exothermic peak can clearly be seen for not only the differential, but also for the ordinary graph, which speaks of the conversion of the unstable amorphous PbC_2O_4 into the stable crystalline form with the evolution of excess internal energy.

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* The decomposition of copper oxalate proceeds according to the equation $CuC_2O_4 = Cu + 2CO_2$. The copper that separates is partially oxidized. ** Freshly precipitated PbC_2O_4 was separated and dried at 110° for one hour.

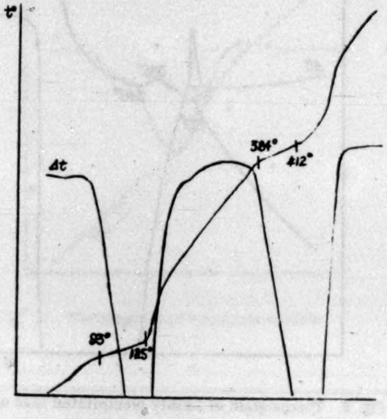

Fig. 4. Thermogram of manganese oxalate.

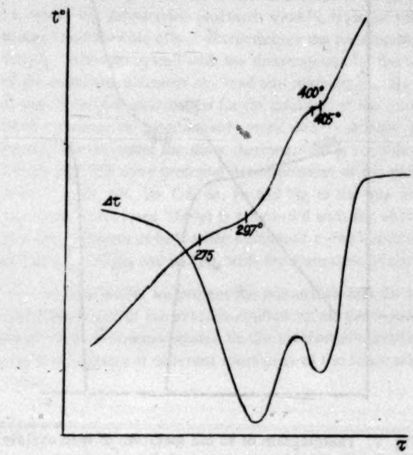

Fig. 5. Thermogram of nickel oxalate.

TABLE

Substance	Temperature interval		Solid decomposition products
	Removal of water	Decomposition of oxalate	
$H_2C_2O_4 \cdot 2H_2O$	96–99°	191–196°	–
$NiC_2O_4 \cdot 2H_2O$	275–295	400–405	Ni
$CoC_2O_4 \cdot 2H_2O$	219–233	400–409	Co
$FeC_2O_4 \cdot 2H_2O$	214–200•	371–379	Fe
$MnC_2O_4 \cdot 2H_2O$	93–125	384–412	MnO
$ZnC_2O_4 \cdot 2H_2O$	188–230	414–426	ZnO
$MgC_2O_4 \cdot 2H_2O$	196–212	421–419•	MgO
$CdC_2O_4 \cdot 3H_2O$	106–116	368–398	Cd + CdO
PbC_2O_4	–	354–318•	PbO
SnC_2O_4	–	350–342•	SnO_2
$CaC_2O_4 \cdot H_2O$	105–110	263–285	$CaCO_3$
$SrC_2O_4 \cdot H_2O$	122–164	182–194	$SrCO_3$
BaC_2O_4	–	226–246	$BaCO_3$
HgC_2O_4	–	233–320	Hg + HgO
$CuC_2O_4 \cdot 2H_2O$	140–171	320–376	Cu + CuO

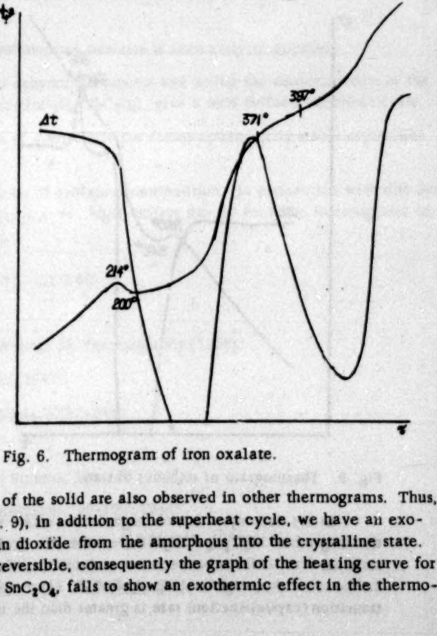

Fig. 6. Thermogram of iron oxalate.

Similar transitions from the unstable to the stable state of the solid are also observed in other thermograms. Thus, for example, in the case of the heating curve for SnC_2O_4 (Fig. 9), in addition to the superheat cycle, we have an exothermic effect (541-566°) for the transition of the liberated tin dioxide from the amorphous into the crystalline state. It is self-understood that this process is thermodynamically irreversible, consequently the graph of the heating curve for very slowly cooled SnO_2, obtained from the decomposition of SnC_2O_4, fails to show an exothermic effect in the thermogram.

• Presence of superheating.

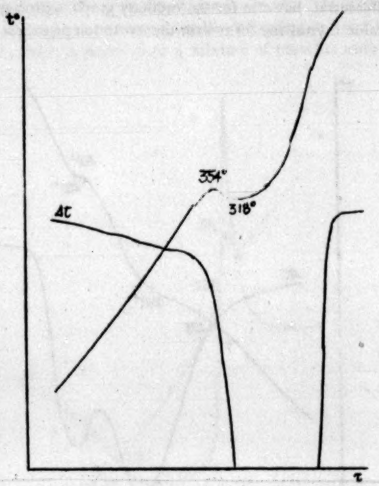

Fig. 7. Thermogram of an old specimen of lead oxalate.

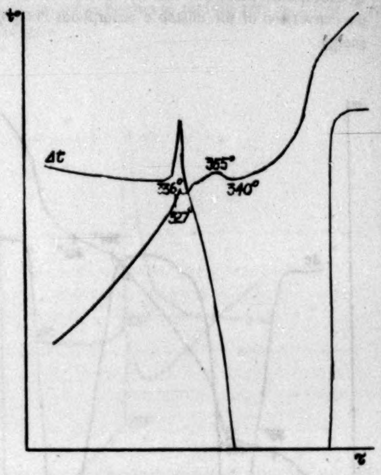

Fig. 8. Thermogram of freshly precipitated lead oxalate.

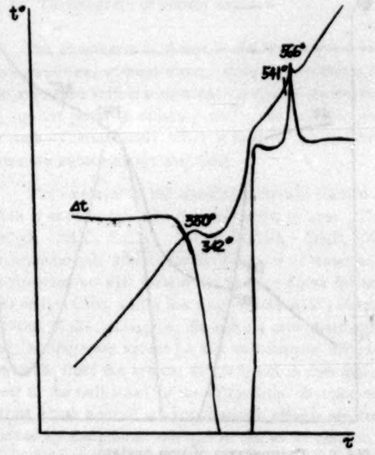

Fig. 9. Thermogram of stannous oxalate.

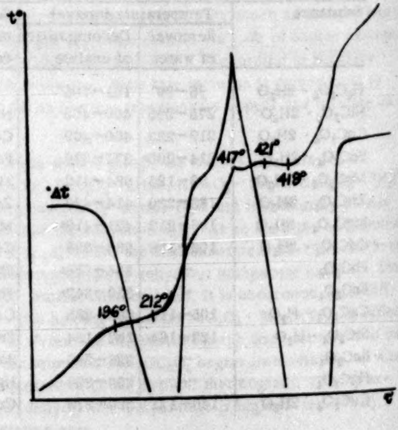

Fig. 10. Thermogram of magnesium oxalate.

In the decomposition of magnesium oxalate we have an interesting example of unstable solid formation. In the thermogram of $MgC_2O_4 \cdot 2H_2O$ the exothermic peak for the transition from unstable anhydrous salt into the stable (crystalline) form is fixed between two endotherms, after which the thermal decomposition of MgC_2O_4 takes place (Fig. 10). In the other thermograms (Fig. 4, 5, 7, 8, 11) the amorphous stage cannot be detected, probably for the reason that the transition (crystallization) rate is greater than the thermal decomposition rate [8].

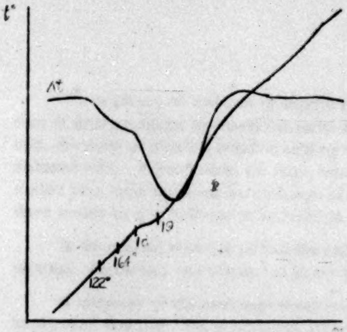

Fig. 11. Thermogram of strontium oxalate.

The oxalates of the alkaline earth metals, suffering thermal dissociation into carbon monoxide and the metal carbonates, also give singular type thermograms.

The heating curve for strontium oxalate is shown in Fig. 11, where the dehydration process is weakly depicted while a distinct endothermic effect characterizes the decomposition of SrC_2O_4. When compared with the thermograms for the oxalates of the transition elements tin, lead and magnesium, the thermal decomposition endotherms for the oxalates of the alkaline earth elements are incomparably more weakly defined on the heating curves (under the same thermographing conditions). Apparently, the more profound decomposition of the oxalates of Fe, Co, Ni, Mn, Zn, Cd, Sn, Pb and Mg to the free metals and metal oxides (see Table) is associated with the absorption of a large amount of heat when compared to the decomposition of CaC_2O_4, SrC_2O_4 and BaC_2O_4 with the formation of carbonates.

In conclusion, we present the numerical data for the thermal dissociation of the oxalates studied by us, the reproducibility of which was demonstrated by the method of comparing several thermograms of different specimens of the same salt (see Table).

SUMMARY

1. The thermographic method was used to characterize the oxalates of the bivalent metals Ni, Co, Fe, Mn, Zn, Cd, Mg, Pb, Sn, Ca, Sr, Ba, Hg, Cu and the dihydrate of oxalic acid.

2. The endothermic and exothermic type of heating curves for the thermal decomposition of bivalent metal oxalates was established.

3. It was observed that the decomposition of copper and mercury oxalates is autocatalytic in nature.

4. It was shown that superheating is present in both the dehydration process and during the decomposition of the anhydrous salts. The oxalates without water of crystallization (SnC_2O_4, PbC_2O_4), give a well defined superheat cycle.

5. The irreversible transformation of the unstable form of a solid into the thermodynamically stable crystalline state was observed in a number of cases.

6. The form of the thermograms depends on the character of oxalate decomposition. In connection with this the thermogram for the decomposition of magnesium oxalate ($MgC_2O_4 \rightarrow MgO$) differs sharply from the thermograms for the oxalates of the alkaline earth metals ($MC_2O_4 \rightarrow MCO_3$).

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EXCHANGE OF RADICALS BETWEEN ORGANIC COMPOUNDS IN SOLUTION

I. P. Gragerov

The mobility of radicals in organic compounds determines to a large degree their chemical behavior. The ease of their exchange reactions can serve as a measure of radical mobility, whence such reactions of similar radicals, the study of which is possible only by means of the isotopic method, give the rules for mobility in the least distorted form. In contrast to the large number of studies made on the exchange of hydrogen isotopes, only a few studies have been made on the exchange of similar alkyl or aryl radicals between different organic molecules. Only three studies in this field are to be found in the literature [1].

In the present work we studied the exchange of methyl, ethyl and phenyl residues between two compounds in solution. Deuterium was substituted in one of the components of the radical exchange reaction.

A summary of the exchange experiments is given in the Table. From the presented data it can be seen that heavy ethyl bromide fails to exchange its ethyl radicals with either phenetole or ethyl acetate, even under drastic conditions. The same is true with respect to the exchange of phenyl groups between heavy iodobenzene and anisole.

A considerable degree of exchange even under the mildest conditions is observed between ethyl bromide and ethyl iodide, but not between the latter and phenetole. Ethyl bromide exchanges even more easily with diethyl sulfate.

Heavy dimethyl sulfate readily exchanges the methyl radicals with methyl iodide and methyl acetate, but not with the methyl ester of p-toluenesulfonic acid. On the other hand, the latter compound quite readily exchanges with methyl iodide. Exchange between methyl iodide and anisole is not observed under these conditions.

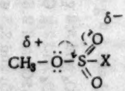
In the presence of acetic acid there is an exchange of radicals between ethyl bromide and ethyl acetate. The exchange between these two compounds proceeds in nitrobenzene medium, which apparently is explained by the presence of acetic acid formed as a result of decomposition of the reaction mixture. (Acetic acid was isolated by us in these experiments).

The presence of anhydrous aluminum bromide fails to lead to exchange between phenetole and ethyl bromide. The loss of deuterium by heavy ethyl bromide in these experiments is associated with its dilution by the light compound, formed in accord with the equation [2].

$$C_6H_5OC_2H_5 + AlBr_3 \rightarrow C_6H_5OAlBr_2 + C_2H_5Br.$$

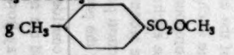
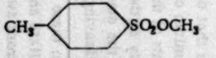
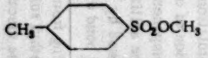
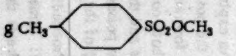
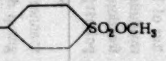
An explanation of all of the above given data from one viewpoint presents certain difficulties. The most probable is the postulation that the exchange proceeds through the intermediate formation of onium compounds. The ease of formation of onium compounds, which also means the ease of exchange, should be determined by the properties of both components of the exchange reaction – the ability of one of them (acceptor) to add the positively charged residues and the ability of the second (donor) to give them away. The acceptor properties depend on the degree of freedom possessed by the electron pairs of the onium atom former; the donor properties depend on the degree of polarity of the bond cleaving the positively charged residue.

Proceeding from these considerations, it becomes possible to satisfactorily explain our results in the following manner: dimethyl sulfate and the methyl ester of p-toluenesulfonic acid are poor acceptors, inasmuch as the SO_2 group draws the electrons away from oxygen.



This structural characteristic makes them excellent donors. Absence of methyl group exchange between these compounds is due to the fact that they cannot form an oxonium compound with each other. Rather, they should readily undergo exchange with good acceptors, i.e., according to the scheme:

Conditions and Results of the Exchange Experiments

Exchanging Compounds	Temperature	Time (in hours)	Excess density of the water from the combustion (γ)				Per cent of exchange*
			of the starting heavy compound	calculated for the exchange radicals of both components in the equilibrium reaction	Found		
					in the heavy component	in the exchange radical of the light component	
4.5 g C_2D_5Br and 4.9 g $C_6H_5OC_2H_5$	193*	40	1817	900	1770	8	–
4.3 g C_2D_5Br and 4.6 g $CH_3COOC_2H_5$	193	40	1817	780	1770	30	–
3.7 g C_2D_5Br and 5.9 g C_2H_5I	193	9	1817	860	1544	226	26
2.5 g C_2D_5Br and 3.1 g $(C_2H_5)_2SO_4$	153	10	973	335	–	206	58
4.6 g C_2D_5Br and 4.4 g $CH_3COOC_2H_5$ with 12 g $C_6H_5NO_2$	193	40	1817	830	–	270	33
3.8 g C_2D_5Br and 4.4 g $CH_3COOC_2H_5$ with 10 g $C_6H_5NO_2$	198	37	1817	750	–	330	44
2.1 g C_2D_5Br, 3.2 g $CH_3COOC_2H_5$ and 0.6 g CH_3COOH	194	40	973	340	–	210	62
5 g C_2D_5Br, 6.5 g $C_6H_5OC_2H_5$ and 3.4 $AlBr_3$	20	2	1817	845	1747	20	–
3 g C_2D_5Br, 5.2 g $C_6H_5OC_2H_5$ and 4.4 g $AlBr_3$	62	22	973	375	580	24	–
3.7 g C_2D_5I and 4 g $C_6H_5OC_2H_5$	156	29	1118	480	1138	6	–
4.6 g CD_3I and 6.1 g $C_6H_5OCH_3$	156	29	1593	578	–	6	–
10.2 g C_6D_5I and 5.9 g $C_6H_5OCH_3$	180 200	15 4	1480	881	1400	26	–
2 g $(CD_3)_2SO_4$ and 5.2 g CH_3I	150	6	546	250	292	215	86
2 g $(CD_3)_2SO_4$ and 2 g CH_3COOCH_3	154	6	546	290	270	270	93
2.3 g $(CD_3)_2SO_4$ and 2.6 g CH_3COOCH_3	125	7.5	672	342	507	202	59
2 g $(CD_3)_2SO_4$ and 2.5 g CH_3COOCH_3	99	10	672	317	654	58	18?
2 g $(CD_3)_2SO_4$ and 2 g CH_3COOCH_3	61	4	546	288	522	24	–
2.3 g $(CD_3)_2SO_4$ and 3.4 g 	99	13	672	474	715	35	–
3 g $(CD_3)_2SO_4$ and 4.5 g 	126	8	672	452	703	47	–
2.4 $(CD_3)_2SO_4$ and 4.2 g 	156	6	672	419	666	23	–
3.3 g $(CD_3)_2SO_4$ and 3.9 g 	156	10	687	488	639	57	12?
3.8 g CD_3I and 4 g 	156	10	1593	689	1290	270	39

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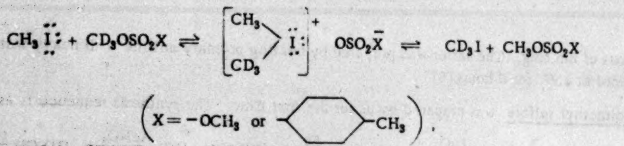
* Based on the amount of deuterium in the light component of the exchange reaction.

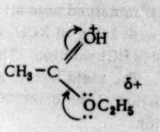


(1)

which scheme also explains the exchange with methyl iodide and methyl acetate.

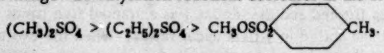
Ethyl bromide fails to exchange with phenetole and ethyl acetate because of insufficient polarity. For the same reason there is no exchange between methyl iodide, ethyl iodide and iodobenzene, on the one hand, and anisole and phenetole on the other. In the exchange with diethyl sulfate the ethyl bromide apparently functions as the acceptor, and the reaction proceeds in accord with an analogous scheme [1]*

The catalytic influence of acetic acid on the exchange between ethyl bromide and ethyl acetate can be explained by the increase in the donor ability of one of the components in the reaction, probably the ethyl acetate, under the influence of the added proton (see scheme).



The absence of exchange between ethyl bromide and phenetole in the presence of aluminum bromide is probably explained by the fact that all of the aluminum bromide is combined with the phenetole in a stable complex, and consequently the compound $\overset{\delta+}{C_2H_5}-\overset{\delta-}{AlBr_4}$, cannot be formed, which, if it were present in the mixture, should readily exchange its ethyl groups with phenetole.

The unquestionable bond existing between the ease of radical exchange and the alkylation tendency should be mentioned: the ease of the exchange and alkylation reactions decreases in the order



On the basis of this relationship it is natural to assume that kindred mechanisms prevail for both types of reactions, and to consider the donor properties of the alkylating agent and the acceptor properties of the substance being alkylated as playing an important role also in alkylation reactions.

EXPERIMENTAL

Heavy ethyl bromide was obtained by the addition of heavy hydrogen bromide to ethylene, using the method proposed by Gustavson [3], under the conditions worked out for light substances [4]. Into a solution of 11 g of anhydrous aluminum bromide in 6.5 g of ethyl bromide, cooled to −78° with a mixture of solid carbon dioxide and acetone, was rapidly passed a dry mixture of heavy hydrogen bromide and ethylene, cooled down to the same temperature (the ethylene was taken in slight excess).

Hydrogen bromide was obtained from dilute heavy water, red phosphorus and bromine. The usual method was changed for the sake of water economy: for 17.4 g of phosphorus was taken 28.5 g of water and 180 g of bromine. The hydrogen bromide was purified from bromine in a tube filled with broken glass and a mixture of 1 g of red phosphorus with 1 g of heavy water. The reaction mass and purification system at the end of the operation were heated with a burner. The gas was dried over calcium chloride that had been heated at 400°, and prior to entering the reaction vessel it was passed through a gas meter containing nitrobenzene.

The crude ethyl bromide was treated with ice, washed with soda water, again with water and then dried over calcium chloride. The yield was 63% of the theoretical, based on water taken. Fractional distillation gave the pure substance, b.p. 38.0-38.5° at 764 mm and d_4^{20} 1.4586.

Heavy ethyl iodide was prepared by the reaction worked out for light substances [5]. The mixture of equivalent amounts of heavy ethyl bromide and methyl iodide was heated for several hours with a small amount of anhydrous aluminum chloride. The addition of fresh $AlCl_3$ was made 3-4 times during the heating period. The reaction mixture was treated with water, the lower layer was separated, washed with alkali, water, dried and distilled. The obtained ethyl iodide had b.p. 69.5-72° at 739 mm and d_4^{20} 1.9393.

Heavy iodobenzene was obtained by the usual method from aniline containing deuterium in the ortho- and para- positions of the ring. The latter was prepared by heating ordinary aniline with heavy water and a small amount of sulfuric acid at 150° for 6 hours [6].

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* Proceeding from the developed considerations, the exchange between ethyl bromide and ethyl iodide is explained with difficulty. It is quite possible that the exchange depends on the dissociation of the iodide into the $C_2H_5^{\cdot}$ radical and atomic iodine.

Heavy dimethyl sulfate was prepared by us for the first time. The synthesis sequence is as follows:

$$CH_3NO_2 \xrightarrow{D_2O} CD_3NO_2 \xrightarrow[HCl]{Fe} CD_3NH_2 \cdot HCl \xrightarrow{AgNO_2} CD_3OH \xrightarrow{oleum} (CD_3)_2SO_4.$$

50 g of nitromethane was heated in an ampoule for 12 hours at 98° with 1.4 g of D_2O (99.6%), 1 g of anhydrous sodium acetate, and 1 g of glacial acetic acid [7]. The water layer was then separated, and the nitromethane without purification was used for reduction. The amount of deuterium in the combustion water from nitromethane was 6200 γ (instead of calculated 5700 γ).

The nitromethane was reduced by the method [8] already used for the preparation of heavy methylamine [9]. To 50 g of nitromethane was added 120 ml of boiled water and 170 g of iron turnings. The air from the apparatus was displaced with hydrogen and in a stream of hydrogen, with mixing, there was added 110 ml of concentrated hydrochloric acid at such a rate that the temperature failed to rise above 70° and the reaction mass remained acid all of the time. The reaction mass (having lost the odor of nitromethane) was then made alkaline with 100 g of KOH, and the methylamine was steam distilled (about 1 liter of distillate) into a receiver containing 20% HCl solution. The obtained solution of methylamine hydrochloride was evaporated to dryness on the water bath. The yield was 45 g. The amount of deuterium in the combustion water was 3980 γ. The loss of a considerable portion of the deuterium is explained by the reaction of nitromethane with hydrochloric acid and water during reduction.

Heavy methylamine was converted into heavy methyl alcohol by the method developed for light substances [10]. With ice cooling 44 g of heavy methylamine hydrochloride was ground with 111 g of silver nitrate and 30 ml of water. The liquid was suction filtered and the residue was extracted five times with water. The water extract was acidified with 5% sulfuric acid and boiled in a flask under reflux. When the evolution of nitrogen slackened, new portions of acid were added. The boiling was continued until gas evolution ceased.* The reaction mass was then distilled from a flask fitted with a long column. The fraction, distilling at 96-99.5° at 753 mm, in amount 200 ml, was saturated with potash and distilled. The single repetition of such a fractional distillation gave 7.2 g of methyl alcohol. The yield was 34% of the theoretical (b.p. 65-67°). As was shown by analysis, there was no loss of deuterium in this stage.

Heavy dimethyl sulfate was prepared from heavy methyl alcohol by the method developed for light substances [11]. To 17.6 of methyl alcohol with ice cooling there was gradually added, with shaking, 79 g of 60% oleum, and the reaction mixture was distilled in vacuum. A second fractional distillation in vacuum gave 23.4 g of pure dimethyl sulfate, which after shaking with MgO to alkaline reaction, distilled at 104-104.5° at 46 mm, d_4^{20} 1.3257. The yield was 66% of the theoretical. There was no loss of deuterium in this stage also.

Heavy methyl iodide. Modifications were introduced into the usual method for the preparation of this substance in the interest of maximum utilization of the heavy alcohol: for 7.3 g of alcohol there was taken 3 g of red phosphorus and 33 g of iodine, which permitted increasing the yield of CD_3I up to 25 g (77%). The constants of the substance, used in the experiments, were as follows: b.p. 41-41.5° at 744 mm, d_4^{20} 2.276.

Exchange experiments. The weighed mixture of heavy and light substances was sealed in a glass ampoule and heated for a definite period of time at the given temperature. In some of the experiments, in addition to the components undergoing exchange, the ampoule contained nitrobenzene, acetic acid, or aluminum bromide. The contents of the ampoule were separated into components by fractional distillation. In the experiments with dimethyl sulfate, diethyl sulfate, methyl ester of p-toluenesulfonic acid, and in part of the experiments with anisole and phenetole the fractional distillation was performed in vacuum. In the experiments with aluminum bromide the reaction mixture was treated with ice, the separated lower layer was washed with water, 10% alkali, again with water and then dried prior to distillation.

With the aid of the density determination method we assured ourselves as to sufficient purity of the isolated substances, the density values for which revealed that the presence of other components of the exchange reaction did not exceed 0.5-2%.

The substances isolated in the above described manner were burned over copper oxide and the obtained combustion waters, after adding a small amount of alkali, were analyzed for deuterium content by the microflotation method with an accuracy to 3%.

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* The evolved gas, in addition to nitrogen, contained methyl nitrite, which was removed by liquid air cooling. Heavy methyl alcohol was obtained from this product by heating it in a sealed tube with KOH solution.

A comparison of Column 4 with Columns 6 and 7 in the Table reveals that a satisfactory deuterium balance was obtained in all of the experiments, which fact supports the validity of the analyses.

I am indebted to A. I. Brodsky for his assistance in the work.

SUMMARY

1. The isotopic method was used for studying the exchange of similar ethyl, methyl and phenyl radicals between a number of organic compounds with heating of their mixtures, and also their mixtures with certain additives.

2. The obtained data are explained on the basis of postulating that the exchange proceeds through the intermediate formation of onium compounds.

3. A parallelism was found to exist in the ease of exchange reactions and of alkylation reactions, indicating their kindred mechanism.

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PHYSICO-CHEMICAL ANALYSIS OF BINARY SYSTEMS FORMED BY UREA WITH PHENOLS. IV.

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Along with other methods, the physico-chemical analysis method is currently finding use in solving the problems of mutual atomic influence in molecules. The use of this method makes it possible to establish the facts of chemical reactivity between components in those cases where other study methods prove to be powerless.

If in the study one component remains constant, while the second components differ from each other only by individual atoms, then as a first approximation the changes in the system can be regarded as being due to the influence of this atom on the organic molecule as a whole.

It was shown by us in earlier published papers that urea with phenol gives an unstable compound that is completely dissociated in the liquid phase [1]. A second hydroxyl group in the nucleus leads to the formation of a more stable urea compound with dihydric phenols but of different composition than the compound with phenol; the stability of these compounds changes with change in the position of the second hydroxyl group [2]. The molecular compounds of urea with hydroquinone and of urea with resorcinol, undergoing intramolecular reaction, give a new ternary compound [3].

In the present study we investigated the systems formed by urea on the one hand, and p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitriphenol on the other. These investigations were made for the purpose of elucidating the influence of the position and number of nitro groups in the phenol molecule on the character of reaction with urea.

The melting, density, viscosity, and electrical conductivity methods were used to study the system. The method was described earlier [1]; measurements in the liquid phase were made at three temperatures. The concentrations were always expressed in mole per cent, the viscosity in centipoises.

The hydroxyl hydrogen of phenol is probably the reactive site in the formation of urea compounds with the earlier investigated phenols. When nitro groups are present in the phenol nucleus it is possible to have compound formation as the result of these nitro groups.

To solve this problem we undertook a study of the systems that are formed when urea is reacted with nitrobenzene, p-nitrotoluene, and o-nitrotoluene. Separation in these systems was observed at all concentration ranges.

The system urea-p-nitrophenol was studied by the melting method by Kremann and Rodinis [4], who established the presence of a 1 : 1 compound. We repeated the melting study, and also investigated the density, viscosity, and electrical conductivity at 120, 130, and 140°.

After repeated recrystallization from water the urea used in the study had m.p. 132.7°. After two recrystallizations from alcohol the C.P. p-nitrophenol had m.p. 113.2°.

Our data on melting, given in Fig. 1, differ somewhat from the data of Kremann. The melting temperature of compound $CO(NH_2)_2 \cdot C_6H_5O_3N$ is 116.2°. The eutectic points at 70 and 20 mole % of urea have m.p. 110.7 and 91.5°, respectively.

The viscosity curves (Fig. 2) rise quite sharply from urea, pass through a maximum at 50-60 mole % urea, and descend to p-nitrophenol. With elevation of the temperature the maximum shifts toward the urea side. The temperature coefficient of the viscosity is also greatest in the region corresponding to 50 mole %.

The isotherms of the density are shown in Fig. 3, appearing as curves that are slightly convex to the composition axis.

The isotherms of the electrical conductivity (Fig. 4), slowly rising from the electrical conductivity of p-nitrophenol, begin to rise more rapidly at 70 mole % urea, and for the isotherms at 140° they pass through a maximum in the region of 90 mole % urea.

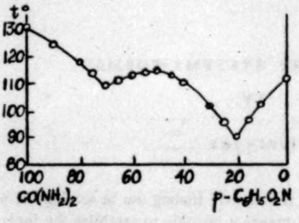

Fig. 1. Melting point curve of the system urea-p-nitrophenol.

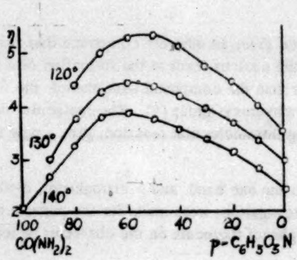

Fig. 2. Viscosity curves of the system urea-p-nitrophenol.

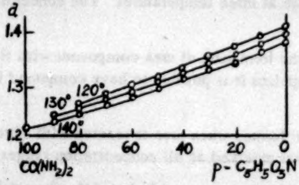

Fig. 3. Density curves of the system urea-p-nitrophenol.

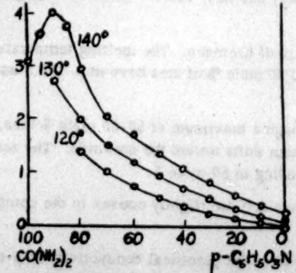

Fig. 4. Electrical conductivity curves of the system urea-p-nitrophenol.

Correcting the electrical conductivity for viscosity ($\eta\kappa$), as is to be expected, makes the isotherms somewhat straighter in the region of 70 mole % urea, but it fails to change the general course of the curve (Fig. 5). The maximum is found at 90 mole % urea and for the 140° isotherms it corresponds to $\eta\kappa = 10.88 \cdot 10^4$ (for urea $\eta\kappa = 6.42 \cdot 10^4$).

System urea-o-nitrophenol was studied by the melting method by Kremann and Rodinis [4]. The occurrence of stratification was established by them. Our attempts to study this system in the liquid phase proved unsuccessful, inasmuch as we were unable to get complete miscibility even with considerable increase in temperature.

System urea-2,4-dinitrophenol was studied by the melting method by Puschin and Rikowski [5]. They obtained a curve with a eutectic and made the conclusion that chemical interaction between the components is absent in the system. We repeated the melting study, and also investigated the viscosity, density, and electrical conductivity at 120, 130, and 140°.

Chemically pure dinitrophenol was taken for the study, which after recrystallization from benzene had m.p. 114.7°.

The melting point curve for the system is shown in Fig. 6. The curve consists of three branches – two branches showing the crystallization of the pure components and one branch showing the crystallization of the compound $2CO(NH_2)_2 \cdot C_6H_4O_5N_2$ with m.p. 116.4°. The eutectic points with m.p. 112.5 and 95° respectively have the composition 80 and 40 mole % urea. The sharp difference from the melting curve obtained by Puschin and Rikowski is explained by the fact that in the region of the maximum exceedingly strong supercooling of the mixtures takes place, reaching a value of 20-30°. Only as the result of vigorous stirring and seeding were we able to produce a maximum on the curve, which at first escaped us also.

The viscosity isotherms (Fig. 7) have a maximum in the region of 75 mole % urea, which with elevation of the temperature shifts slightly toward the urea side (up to 78 mole %). The convexity of the isotherms to the composition axis in the region rich in dinitrophenol indicates the dissociation of its associated molecules.

The density curves (Fig. 8) are straight lines, and only the 140° isotherm is slightly convex to the compsoition axis.

The electrical conductivity curves (Fig. 9), as in the previous system, have a maximum in the region rich in urea; thus, for the 130° isotherm it is found at 80, and for the 140° isotherm at 85 mole % of urea. It might be thought that displacement of the maximum up to 85 mole % of urea occurred as the result of a lower viscosity in this region. Actually, on the electrical conductivity curves corrected for viscosity, which are shown in Fig. 10, the maximum for both the 130° and 140° isotherms is found at 80 mole % urea. In contrast to the system urea-p-nitrophenol (Fig. 5), the difference between $\eta\kappa$ maximum ($73.78 \cdot 10^4$) for 140° and $\eta\kappa$ urea ($6.86 \cdot 10^4$) is considerably greater. Partial decomposition takes place when the mixtures are heated above 150°.

System urea-2,4,6-trinitrophenol. Chemically pure picric acid was used in the study, which after recrystallization from alcohol had m.p. 121.8°.

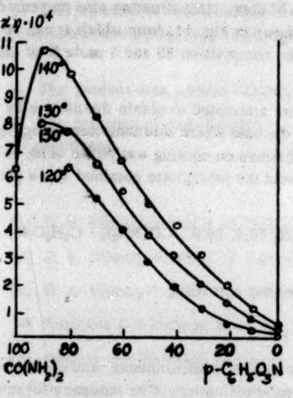

Fig. 5. Electrical conductivity curves, corrected for viscosity, of the system urea-p-nitrophenol.

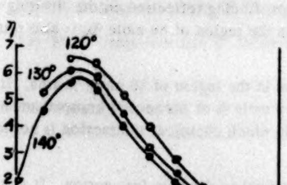

Fig. 7. Viscosity curves of the system urea-2,4-dinitrophenol.

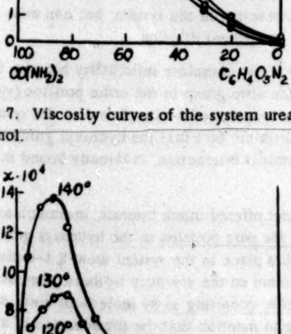

Fig. 9. Electrical conductivity curves of the system urea-2,4-dinitrophenol.

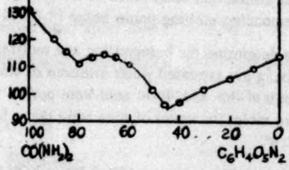

Fig. 6. Melting point curve of the system urea-2,4-dinitrophenol.

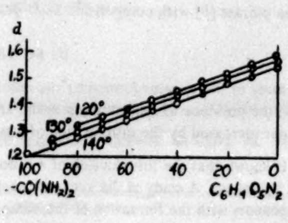

Fig. 8. Density curves of the system urea-2,4-dinitrophenol.

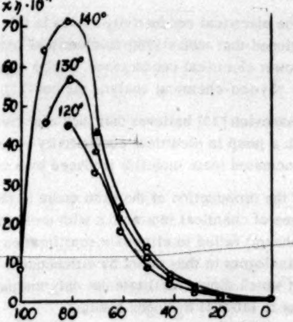

Fig. 10. Electrical conductivity curves, corrected for viscosity, of the system urea-2,4-dinitrophenol.

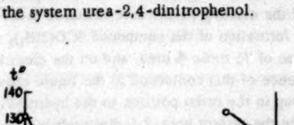

Fig. 11. Melting point curves of the system urea, 2,4,6-trinitrophenol.

We were unable to make a sufficiently full study of the melting of the system due to the fact that decomposition is encountered for the mixtures that contain from 70 to 20 mole % of urea. This situation also prevented us from studying the system in the liquid phase. Part of the melting curve is shown in Fig. 11, from which it can be seen that chemical interaction takes place in the system. The eutectics have the composition 83 and 5 mole % of urea with the corresponding melting points being 97.8 and 116.7°.

To determine the composition and melting point of the picrate we attempted to obtain the picrate by the method of mixing hot saturated water solutions of urea and picric acid. In the case where solutions containing equimolecular amounts of urea and picric acid were poured together the product obtained on cooling was picric acid; in the case where two moles (or more) of urea were taken for one mole of picric acid the precipitate obtained was a picrate with m.p. 150.6°.

0.640, 0.874 g sub.: 0.126, 0.172 g KOH [7]. Found %: $C_6H_4O_7N_3$ 80.9, 80.8. $CO(NH_2)_2 \cdot C_6H_4O_7N_3$. Calculated %: $C_6H_4O_7N_3$ 79.3.

The picrate [6] with composition 1 : 1, described in the literature, has m.p. 142°.

DISCUSSION OF RESULTS

A study of the systems formed by the reaction of urea with nitrobenzene, p-nitrotoluene, and o-nitrotoluene reveals that the presence of a nitro group in the aromatic nucleus leads to stratification. The tendency for mutual solubility is not increased by the introduction of a second nitro group [8].

It is known that the introduction of a nitro group into phenol results in considerably increased mobility of the hydroxyl hydrogen. A study of the system urea-p-nitrophenol revealed that chemical interaction takes place between the components with the formation of the compound $CO(NH_2)_2 \cdot C_6H_5O_3N$, finding reflection on the melting curves. This compound, judging from the viscosity curves, having a maximum in the region of 50 mole %, is also retained in the liquid phase.

The electrical conductivity curves in this system have a maximum in the region of 90 mole % urea. It should be mentioned that such a jump in electrical conductance on adding 5-15 mole % of the second component, usually with a lower electrical conductance, is also observed for those systems in which chemical interaction is not revealed by other physico-chemical analysis methods [9].

Usanovich [10] believes that such electrical conductivity curves indicate acid-base interaction. It seems to us that such a jump in electrical conductivity is not always produced by interaction in the system, but can arise as the result of increased ionic mobility produced by a certain degree of second component dilution.

If the introduction of the nitro group in the para position not only led to complete miscibility but also increased the degree of chemical interaction with urea, then the introduction of the nitro group in the ortho position (system urea-o-nitrophenol) failed to eliminate stratification in the system. That the behavior of o-nitrophenol in the system with urea is analogous to that shown by nitrobenzene is probably associated with the fact that the hydroxyl group, the presence of which should facilitate not only mutual solubility but also chemical interaction, is already bound in the nucleus due to internal hydrogen bonding.

In connection with this a study of the system urea-2,4-dinitrophenol offered much interest, inasmuch as in this case one of the nitro groups is in the ortho position and the second is in the para position to the hydroxyl group. A study of the melting point curve revealed that chemical interaction takes place in the system urea-2,4-dinitrophenol with the formation of the compound $2CO(NH_2)_2 \cdot C_6H_4O_5N_2$. The maximum on the viscosity isotherm, occurring in the region of 75 mole % urea, and on the electrical conductivity isotherm, occurring at 80 mole % of urea, confirmed the presence of this compound in the liquid phase also. It is interesting to mention that the introduction of a second nitro group in the ortho position to the hydroxyl (into p-nitrophenol) changed the composition of the obtained compound. In the system urea-2,4-dinitrophenol the prolonged heating above 150° of mixtures analyzing close to 50 mole % results in gas evolution and the formation of a high melting product that is difficultly soluble in water. An increase in the number of nitro groups to three, as was revealed in the study of the system urea-picric acid, lowers the decomposition temperature of the mixtures; thus, in the 50 mole % region it drops to 110-120°. However, the strength of the chemical union with urea is increased, inasmuch as it is possible to obtain the fairly stable picrate $CO(NH_2)_2 \cdot C_6H_3O_7N_3$.

SUMMARY

1. A study was made of the viscosity, densityy, and electrical conductivity of the systems urea-p-nitrophenol and urea-2,4-dinitrophenol at 120, 130, and 140°, and also of their melting.

2. It was established that chemical interaction is also present in the liquid phase for the system urea-p-nitrophenol with the formation of the compound $CO(NH_2)_2 \cdot C_6H_5O_3N$.

3. The presence of chemical interaction was established in the system urea-2,4-dinitrophenol with the formation of the compound $2CO(NH_2)_2 \cdot C_6H_4O_5N_2$, which found reflection on the curves of all of the investigated properties.

4. The product urea picrate $CO(NH_2)_2 \cdot C_6H_3O_7N_3$ was obtained from water with m.p. 150.6°.

5. The presence of stratification was established in the systems urea-nitrobenzene, urea-o-nitrotoluene, and urea-p-nitrotoluene.

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* Consultants Bureau Translation, p. 59.

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*** Consultants Bureau Translation, p. 1087.

**** Consultants Bureau Translation, p. 575.

2. It was established that chemical interaction is also present in the liquid phase for the system urea-p-nitrophenol with the formation of the compound $CO(NH_2)_2 \cdot C_6H_5O_3N$.

3. The presence of chemical interaction was established in the system urea-2,4-dinitrophenol with the formation of the compound $2CO(NH_2)_2 \cdot C_6H_4O_5N_2$, which found reflection on the curves of all of the investigated properties.

4. The product urea picrate $CO(NH_2)_2 \cdot C_6H_3O_7N_3$ was obtained from water with m.p. 130°C.

5. The presence of stratification was established in the systems urea-nitrobenzene, urea-o-nitrotoluene, and urea-p-nitrotoluene.

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**** Consultants Bureau Translation, p. 576.

POLAROGRAPHIC INVESTIGATION OF HYDROGENATION PROCESSES

IV. HYDROGENATION OF ALLYL ACETATE MIXTURES WITH DI- AND TRISUBSTITUTED ETHYLENE DERIVATIVES

A. L. Markman and A. S. Gorokhovskaya

Lebedev [1], in studying the catalytic hydrogenation process for binary mixtures of unsaturated compounds, established a number of rules. In particular, he established that on all of the hydrogenation curves for mixtures, in which one of the components is a monosubstituted ethylene derivative, there occur sharply defined breaks and two more or less horizontal sections; the monosubstituted ethylene derivatives always hydrogenate first. Making use of contemporary terminology, this rule should be understood to mean that the hydrogenation of such mixtures proceeds selectively with saturation of the monosubstituted ethylene in the first phase.

We chose allyl acetate as the monosubstituted ethylene derivative for our experiments. Allyl acetate fails to give a polarographic wave. Selecting as the second component of the mixture a compound capable of being polarographed, we were able from variation in the wave height of the latter to follow the distribution of hydrogen between both components in the mixture during the whole process [2].

EXPERIMENTAL

In the experiments with allyl acetate-maleic acid and allyl acetate-fumaric acid mixtures we polarographed the samples that were taken during the hydrogenation course, for which purpose we dissolved 1 ml of each sample in 50 ml of 0.1 N HCl in 50% alcohol. In our paper [3] we have already given the conditions for polarographing maleic and fumaric acids in HCl acidified alcohol solution. Striving to separate the half-wave potentials of the two geometric isomers as much as possible during their joint polarographing, we used 95-96% alcohol in the experiments described in our paper [3]. In the present experiments with binary mixtures composed of allyl acetate with each of two stereoisomeric acids we succeeded in polarographing these acids in 50% alcohol solution. In this way for maleic acid we obtained the half-wave potential $\pi_{1/2}$ −0.68 V, and for fumaric acid −0.82 V.

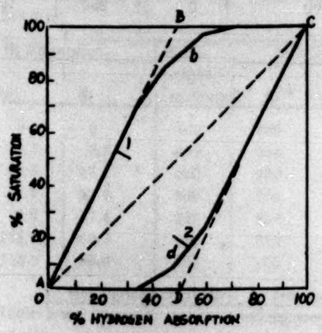

Fig. 1. Hydrogenation of allyl acetate-maleic acid mixture. Catalyst-palladium.
1) Allyl acetate, 2) Maleic acid.

In the given case, as in all of the experiments described below, the series of polarographic curves that were obtained had the same appearance as those shown in Fig. 2 of a previous paper [2]. One of these series of curves obtained by us in our experiments with allyl acetate is given below for the mixture of allyl acetate with mesityl oxide (Fig. 10).

In all of the experiments we took 50 mg of allyl acetate, 210 mg of Al, and 40 ml of alcohol for each experiment; the bath temperature was always kept at 25°.

1. Hydrogenation of allyl acetate-maleic acid mixture in the presence of palladium. The results are summarized in Table 1 and plotted in Fig. 1, where the broken diagonal AC corresponds to the completely nonselective process; the broken lines ABC and ADC correspond to the strictly selective saturation of allyl acetate in the first phase, and of maleic acid in the second phase. Actually, the saturation of allyl acetate proceeds along curve AbC, and that of maleic acid along curve AdC, i.e., with a certain deviation from strict selectivity. The index of selectivity is the ratio of the area of figure AbCdA to the area of the parallelogram ABCD. In the given case this index is S = 0.930. In a parallel experiment the value S = 0.936 was obtained.

The rate of hydrogen absorption by a mixture of allyl acetate and maleic acid is shown in Fig. 2; the arrow indicates the point at which half of the theoretical amount of hydrogen had been absorbed. As is shown by the curve, the absorption rate in the first half of the process is considerably greater than in the second half, i.e., allyl acetate is hydrogenated much faster than maleic acid; however, contrary to the indications of Lebedev, both portions of the curve fail to be horizontal. From the character of both portions of the curve it must be assumed that the saturation of both allyl acetate nnd maleic acid is a first order reaction. The point, close to half saturation (more exactly, the point at which saturation is 46.9%), corresponds to a maleic acid concentration of $230 \cdot 10^{-5}$ mole/liter and allyl acetate concentration of $35 \cdot 10^{-5}$ mole/liter with the initial concentrations of both components being $250 \cdot 10^{-5}$ mole/liter

From this the ratio of the hydrogenation constants of the components in the mixture is equal to

$K = \log \frac{C_0''}{C''} : \log \frac{C_0''}{C''} = 0.042$. Based on the considerations which we expressed earlier [3], for characterizing the degree of process selectivity it is more expedient to use the quantity 1−K as the index. In the given case this index is equal to 0.958, which is sufficiently close to the index obtained by us using the graph method; the latter should be considered as being the more accurate.

TABLE 1

Hydrogenation of Allyl Acetate-Maleic Acid Mixture in the Presence of Pd

Maleic acid 0.58 g, Pd 32 mg. Room temperature 20°. Pressure 722 mm. Theory for hydrogen absorption H_0 253 ml.

H_2 Absorption		Wave height (in mm)	Maleic Acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$ *	$\Delta C \cdot 10^{-5}$ *	Saturation (in %)	$C \cdot 10^{-5}$ *	$\Delta C \cdot 10^{-5}$ *	Saturation (in %)
0	0	380	250	0	0	250	0	0
27.3	10.8	380	250	0	0	196	54	21.6
56.0	22.1	380	250	0	0	139	111	44.4
86.4	34.1	380	250	0	0	79	171	68.4
118.7	46.9	350	230	20	8.0	35	215	86.0
153.3	60.6	290	191	59	23.6	0	250	100
190.3	75.2	188	124	126	50.4	0	250	100
230.1	91.0	68	45	205	82.0	0	250	100
253.0	100	0	0	250	100	0	250	100

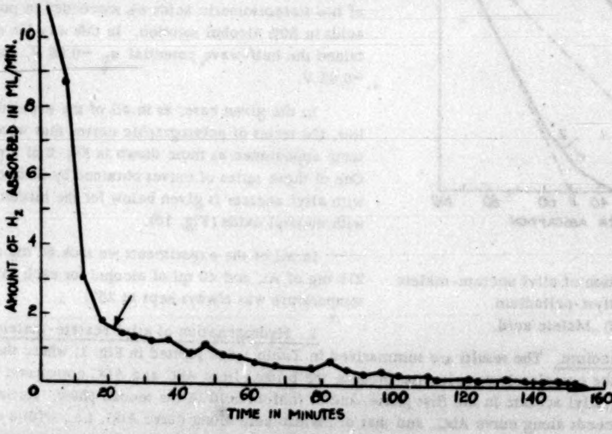

Fig. 2. Hydrogen absorption rate curve for a mixture of allyl acetate and maleic acid. Explanation in text.

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* In this and in the other tables the value C designates concentration, while the value ΔC designates the drop in concentration for each of the components in the mixture. Both values are expressed in moles/liter.

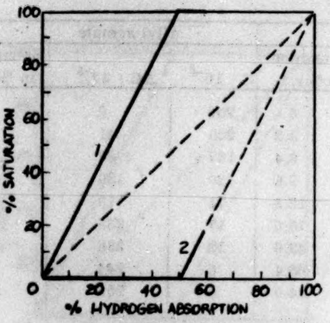

Fig. 3. Hydrogenation of allyl acetate-maleic acid mixture. Catalyst platinum.
1) Allyl acetate, 2) Maleic acid.

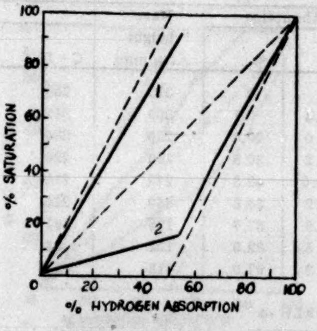

Fig. 4. Hydrogenation of allyl acetate-fumaric acid mixture. Catalyst palladium.
1) Allyl acetate, 2) Fumaric acid.

TABLE 2

Hydrogenation of Allyl Acetate-Maleic Acid Mixture in the Presence of Pt
Maleic acid 0.58 g, Pt 116 mg. Room temperature 14°. Pressure 728 mm. Theory for hydrogen absorption H_0 245.8 ml.

H_2 Absorption		Wave height	Maleic acid			Allyl acetate		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	400	250	0	0	250	0	0
21.3	8.6	400	250	0	0	207	43	17.2
43.5	17.7	400	250	0	0	162	88	35.2
67.0	27.2	400	250	0	0	114	136	54.4
92.0	37.4	400	250	0	0	63	187	74.8
118.7	48.2	400	250	0	0	9	241	96.4
145.0	59.0	330	205	45	18.0	0	250	100

2. Hydrogenation of allyl acetate-maleic acid mixture in the presence of platinum. The results are given in Table 2 and Figure 3. Without making any measurements it can be seen from the figure that the process is strictly selective: the hydrogenation of maleic acid begins after 100% saturation of allyl acetate.

3. Hydrogenation of allyl acetate-fumaric acid mixture in the presence of palladium. The results are given in Table 3 and Figure 4. From the graph we find S = 0.758. In a parallel experiment S = 0.761.

4. The hydrogenation of allyl acetate-fumaric acid mixture in the presence of platinum is shown in Table 4 and Figure 5, the character of the latter being the same as Figure 3. The degree of selectivity is S = 1.0.

5. Hydrogenation of allyl acetate-cinnamic acid mixture in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl solution in 96% alcohol (Table 5 and Figure 6). For this case found S = 0.512. In a parallel experiment S = 0.528. For the sake of comparison we present the calculation of the selectivity index according to Zinovyev [4] (Table 6).

6. Hydrogenation of allyl acetate-cinnamic acid mixture in the presence of platinum. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl solution in 50% ethanol (Table 7 and Figure 7). For this case found S = 0.990.

TABLE 3

Hydrogenation of Allyl Acetate-Fumaric Acid Mixture in the Presence of Pd

Fumaric acid 0.58 g. Pd 64 mg. Room temperature 19°. Pressure 726 mm. Theory for hydrogen absorption H_0 250.8 ml $\pi_{1/2}$ − 0.82 V

H_2 Absorption		Wave height (in mm)	Fumaric acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	310	250	0	0	250	0	0
21.4	9.7	300	242	8	3.2	209	41	16.4
50.0	20.0	290	234	16	6.4	167	83	33.2
77.2	30.8	280	226	24	9.6	120	130	52.0
106.0	42.3	270	218	32	12.8	71	179	71.6
136.9	54.6	260	210	40	16.0	17	233	93.2
169.9	67.7	175	141	109	43.6	12	238	95.2
205.5	82.0	104	84	166	66.4	6	244	97.6
243.3	97.0	18	15	235	94.0	0	250	100

TABLE 4

Hydrogenation of Allyl Acetate-Fumaric Acid Mixture in the Presence of Pt

Fumaric acid 0.58 g, Pt 116 mg. Room temperature 20°. Pressure 720 mm. Theory for hydrogen absorption H_0 253.8 ml.

H_2 Absorption		Wave height (in mm)	Fumaric acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	310	250	0	0	250	0	0
21.1	8.3	310	250	0	0	208	42	16.8
43.3	17.1	310	250	0	0	165	85	34.0
61.8	24.4	310	250	0	0	128	122	48.8
91.8	36.2	310	250	0	0	69	181	72.4
118.5	46.7	310	250	0	0	17	233	93.2
131.9	52.0	298	240	10	4.0	0	250	100

TABLE 5

Hydrogenation of Allyl Acetate-Cinnamic Acid Mixture in the Presence of Pd

Cinnamic acid 0.74 g, Pd 64 mg. Room temperature 20°. Pressure 731 mm. Theory for hydrogen absorption H_0 250 ml. $\pi_{1/2}$ − 1.56 V.

H_2 Absorption		Wave height (in mm)	Cinnamic acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	450	250	0	0	250	0	0
21.1	8.4	420	233	17	6.8	225	25	10.0
43.4	17.4	400	222	28	11.2	191	59	23.6
67.4	27.0	380	211	39	15.6	154	96	38.4
93.5	37.4	340	189	61	24.4	124	126	50.4
120.9	48.4	300	167	83	33.2	91	159	63.6
160.5	60.2	280	154	96	38.4	45	205	82.0
182.2	72.9	220	122	128	51.2	14	236	94.4

7. Hydrogenation of allyl acetate-itaconic acid mixture in the presence of palladium. For polarographing [5], 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 50% ethanol (Table 8 and Figure 8). For the given case S = 0.854. In a parallel experiment obtained S = 0.845.

8. Hydrogenation of allyl acetate-itaconic acid mixture in the presence of platinum. The conditions for polarographing were the same as in the previous experiment (Table 9 and Figure 9). For the given case found S = 0.882.

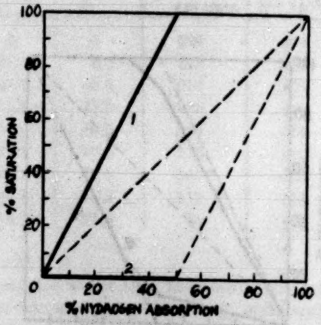

Fig. 5. Hydrogenation of allyl acetate-fumaric acid mixture. Catalyst - platinum.
1) Allyl acetate, 2) Fumaric acid.

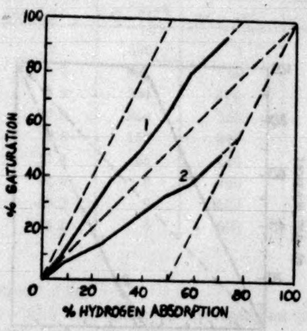

Fig. 6. Hydrogenation of allyl acetate-cinnamic acid mixture. Catalyst - palladium.
1) Allyl acetate, 2) Cinnamic acid.

TABLE 6

Calculation of the Index of Selectivity According to Zinovyev [4]

τ (min.)	Cinnamic acid, C_0 = 250			Allyl acetate, C_0 = 250			K
	C	$\frac{C_0}{C}$	$\log \frac{C_0}{C}$	C	$\frac{C_0}{C}$	$\log \frac{C_0}{C}$	
2	233	1.073	0.03060	225	1.111	0.04571	0.670
4	222	1.126	0.05154	191	1.309	0.11694	0.441
6.5	211	1.185	0.07372	154	1.623	0.21032	0.351
9	189	1.323	0.12156	124	2.016	0.30449	0.408
13.25	167	1.497	0.17522	91	2.747	0.43886	0.399
27.25	156	1.603	0.20493	45	5.556	0.74476	0.276
112.25	122	2.049	0.31154	14	17.86	1.25188	0.257
				Average		0.400	

Index of selectivity 1−K = 0.600

Next we hydrogenated a mixture of allyl acetate with the trisubstituted ethylene derivative – mesityl oxide. As regards the polarographic behavior of mesityl oxide we found only one reference in the literature: according to Adkins and Cox [6], mesityl oxide gives a wave with a half-wave potential of −1.61V, in aqueous NH_4Cl solution and −1.64 V in $N(CH_3)_4OH$.

The polarographing of mesityl oxide was made in 0.1 N NH_4Cl in 50% ethanol. Under these conditions mesityl oxide gives a well defined polarographic wave with a half-wave potential of −1.40 V. The relationship between the wave height and concentration is shown in Table 10.

The values given in Table 10 indicate that a direct relationship exists between the diffusion current and the concentration of the solution.

If should be mentioned that in contrast to cinnamic acid, mesityl oxide fails to give a polarographic wave in a pure alcohol solution of ammonium chloride.

9. Hydrogenation of allyl acetate-mesityl oxide mixture in the presence of palladium. 1 ml of each sample was

dissolved in 50 ml of 0.1 N NH_4Cl in 50% ethanol. The obtained polarograms are shown in Fig. 10, while the results are given in Table 11 and Figure 11. As can be seen from the graph, the index of selectivity is S = 1.0.

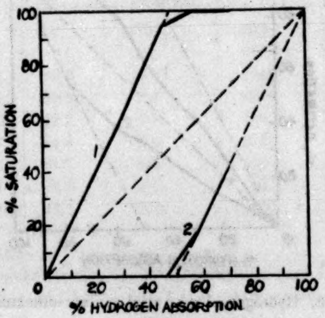

Fig. 7. Hydrogenation of allyl acetate-cinnamic acid mixture. Catalyst platinum.
1) Allyl acetate, 2) Cinnamic acid.

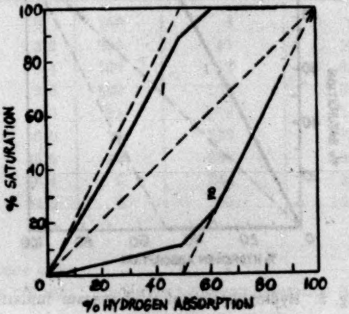

Fig. 8. Hydrogenation of allyl acetate-itaconic acid mixture. Catalyst palladium.
1) Allyl acetate, 2) Itaconic acid.

TABLE 7

Hydrogenation of Allyl Acetate-Cinnamic Acid Mixture in the Presence of Pt

Cinnamic acid 0.74 g, Pt 116 mg. Room temperature 19°. Pressure 725 mm. Theory for hydrogen absorption H_0 251.4 ml. $\pi_{1/2}$ −1.51 V.

H_2 Absorption		Wave height (in mm)	Cinnamic acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	300	250	0	0	250	0	0
21.1	8.4	300	250	0	0	208	42	16.8
43.3	17.2	300	250	0	0	164	86	34.4
66.8	26.6	300	250	0	0	117	133	53.2
91.8	36.5	300	250	0	0	67	183	73.2
118.5	47.1	300	250	0	0	13	237	94.8
147.1	58.5	250	208	42	16.8	0	250	100
177.9	70.8	175	146	104	41.6	0	250	100

10. Hydrogenation of allyl acetate-mesityl oxide mixture in the presence of platinum. The conditions for polarographing were the same as in the previous experiment (Table 12 and Figure 12). For this case S = 0.933.

From an examination of the above experiments it is seen that, in accord with the Lebedev rule, allyl acetate in all cases suffers preferential hydrogenation over di- and trisubstituted ethylene derivatives. However, this preference does not always grow into absolute selectivity.

In mixtures with maleic, fumaric and cinnamic acids the hydrogenation of allyl acetate is absolutely selective in the presence of platinum; in the presence of palladium both components of the mixture suffer simultaneous hydrogenation; however, the hydrogenation rate for allyl acetate is much faster than it is for the disubstituted ethylenic acids. The hydrogenation of allyl acetate-itaconic acid mixtures in the presence of either palladium or platinum bears a similar strictly selective character. In mixtures with the trisubstituted ethylene derivative, mesityl oxide, the hydrogenation of allyl acetate is strictly selective in the presence of palladium and shows a slight deviation from absolute selectivity in the presence of platinum.

TABLE 8

Hydrogenation of Allyl Acetate-Itaconic Acid Mixture in the Presence of Pd

Itaconic acid 0.65 g, Pd 64 mg. Room temperature 12°. Pressure 729.0 mm. Theory for hydrogen absorption H_0 243.8 ml. $\pi_{1/2}$ −0.79 V

H_2 Absorption		Wave height (in mm)	Itaconic acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	220	500	0	0	500	0	0
21.9	9.0	215	489	11	2.2	421	79	15.8
46.1	18.9	210	477	23	4.6	334	166	33.2
70.8	29.0	205	466	34	6.8	244	256	51.2
95.8	39.2	200	455	45	9.0	152	348	69.6
122.5	50.2	195	443	57	11.4	55	445	89.0
155.1	61.9	167	380	120	24.0	0	500	100
181.9	74.5	112	254	246	49.2	0	500	100
214.2	87.8	54	122	378	75.6	0	500	100

TABLE 9

Hydrogenation of Allyl Acetate-Itaconic Acid Mixture in the Presence of Pt

Itaconic acid 0.65 g, Pt 140 mg. Room temperature 14°. Pressure 723.5 mm. Theory for hydrogen absorption H_0 247.4 ml.

H_2 Absorption		Wave height (in mm)	Itaconic acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	220	500	0	0	500	0	0
27.9	11.3	220	500	0	0	387	113	22.6
56.0	22.7	210	477	23	4.6	297	203	40.6
85.8	34.7	205	466	34	6.8	179	321	64.2
117.8	47.6	200	455	45	9.0	69	431	86.2
150.9	61.0	172	390	110	22.0	0	500	100
186.4	75.4	108	247	253	50.6	0	500	100
224.4	90.8	41	93	407	81.4	0	500	100
231.6	93.6	28	64	436	87.2	0	500	100

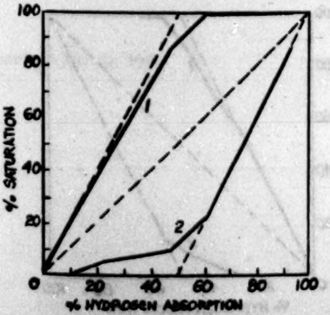

Fig. 9. Hydrogenation of allyl acetate-itaconic acid mixture. Catalyst - platinum
1) Allyl acetate, 2) Itaconic acid.

TABLE 10

Polarographic Indices of Mesityl Oxide

$C \cdot 10^{-3}$ (mole/liter)	h (in mm)	$\frac{h}{C} \cdot 10^4$
5	180	2.6
1	28	2.8
0.5	14	2.8
Average		2.73

TABLE 11

Hydrogenation of Allyl Acetate-Mesityl Oxide Mixture in the Presence of Pd

Mesityl oxide 0.49 g, Pd 64 mg. Room temperature 12°. Pressure 723 mm. Theory for hydrogen absorption H_0 246 ml. $\pi_{1/2}$ −1.37 V.

H_2 Absorption		Wave height (in mm)	Mesityl oxide			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	95	250	0	0	250	0	0
27.3	11.1	95	250	0	0	195	55	22.0
57.1	23.2	95	250	0	0	134	116	46.4
89.1	36.2	95	250	0	0	69	181	72.4
122.4	49.8	95	250	0	0	1	249	99.6
159.3	64.8	67	177	73	29.2	0	250	100
197.5	89.2	38	99	151	60.4	0	250	100
238.3	96.9	6	16	234	93.6	0	250	100
246.3	100	0	0	250	100	0	250	100

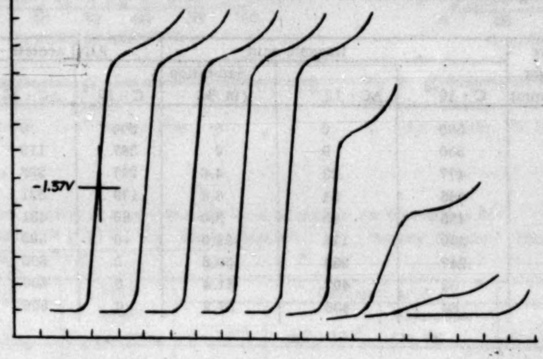

Fig. 10. Hydrogenation polarograms of allyl acetate-mesityl oxide mixture. Catalyst palladium.

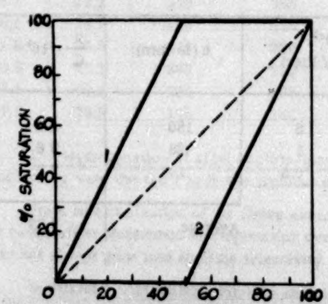

Fig. 11. Hydrogenation of allyl acetate-mesityl oxide mixture. Catalyst palladium.

1) Allyl acetate, 2) Mesityl oxide.

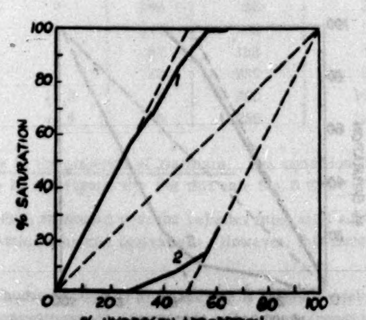

Fig. 12. Hydrogenation of allyl acetate-mesityl oxide mixture. Catalyst platinum.

1) Allyl acetate, 2) Mesityl oxide.

TABLE 12

Hydrogenation of Allyl Acetate-Mesityl Oxide Mixture in the Presence of Pt

Mesityl oxide 0.49 g, Pt 116 mg. Room temperature 25°. Pressure 720 mm. Theory for hydrogen absorption H_0 252.9 ml

H_2 Absorption		Wave height (in mm)	Mesityl oxide			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	120	250	0	0	250	0	0
21.1	8.3	120	250	0	0	209	41	16.4
43.3	17.1	120	250	0	0	164	86	34.4
66.8	26.4	120	250	0	0	118	132	52.8
91.8	36.3	115	239	11	4.4	80	170	68.0
118.5	46.8	110	229	21	8.4	37	213	85.2
147.1	58.2	101	210	40	16.0	0	250	100
157.3	62.2	91	189	61	24.4	0	250	100

SUMMARY

1. With the aid of the polarographic method the hydrogenation processes for binary mixtures of allyl acetate with certain di- and trisubstituted ethylene derivatives were studied. It was established that the Lebedev rule relative to the preferential saturation of the monosubstituted ethylene derivative in the first phase is a first approximation generalization. Depending on the nature of the second component in the mixture and on the catalyst, the degree of selective saturation of the monosubstituted ethylene derivative fluctuates within fairly wide limits (in our experiments from 0.512 to 1.00).

2. The conditions for polarographing mesityl oxide were established, making possible its quantitative determination in solutions.

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POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS

V. HYDROGENATION OF MIXTURES OF DISUBSTITUTED ETHYLENE DERIVATIVES

A. L. Markman

According to Lebedev's observations [1], the symmetrical disubstituted ethylene derivatives are divided into two groups according to their behavior during catalytic hydrogenation: those compounds which, under the conditions of the experiment, are saturated at relatively high rates (11-20 ml of H_2 per minute), and those for which the rate of saturation is considerably less (2-4 ml per minute). To this last category belong compounds in which the double bond is in bilateral conjugation to the benzene ring or to carboxyl. Similar observations were made by Adams [2], Adkins [3] and Kazansky [4].

Of the number of symmetrical disubstituted ethylene derivatives, we studied maleic, fumaric, cinnamic and oleic acids. Hydrogenation experiments of all these acids were carried out under the same conditions: catalyst in the quantity of 32 mg of Pd or 58 mg of Pt per 0.005 mole of acid was introduced; the bath temperature was 25°. We described the technique of hydrogenation, the selection of sample and the polarographic control of the course of saturation earlier [5]. Rate of saturation constants were calculated for each object of investigation from the equation of a first order reaction (Table 1).

Thus, the figures of Table 1 bear out the observations of other authors concerning the fact that oleic acid differs from the other three acids by its considerably higher rate of saturation.

TABLE 1

Reaction Rate Constants of the Catalytic Hydrogenation of Acids

Acids	Catalyst	
	Pd	Pt
Maleic	0.0468	0.0190
Fumaric	0.0067	0.0095
Cinnamic	0.0435	0.0123
Oleic	0.2136	0.0737

Turning to the problem of the hydrogenation of binary mixtures of disubstituted ethylenes, we note the work of Lebedev [1], Yurashevsky [6], Ipatyev [7], Bogdanov and Bashkirova [8], carried out in this direction.

Because of the essential difference of oleic acid from the other three above-named acids, with respect to the nature of substituents, we studied the behavior of binary mixtures, one of the components of which was oleic acid.

If we measure the activity of the double bond by the rate of its saturation, then it can be expected that in mixtures of oleic and maleic acids the oleic will be selectively saturated first. If we assume that both acids are saturated simultaneously, each at its inherent rate, then in this case also the oleic acid should be saturated more rapidly than the maleic. However, the experiment gave no such results.

EXPERIMENTAL

In all the experiments described below we used 210 mg of Al as the carrier, and 40 ml of alcohol as the solvent (with the exception of two experiments); the bath temperature, with the exception of certain indicated cases, was 40°.

1. Hydrogenation of a mixture of oleic and maleic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 96% ethanol [9] (Table 2, Fig. 1). For this experiment an index of selectivity of S = 0.969 was found.

2. Hydrogenation of a mixture of oleic and maleic acids in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 3, Fig. 2). The index of selectivity was S = 0.609.

Thus, we see that the palladium catalyst specifies strict selectivity of the process of hydrogenation of mixtures of maleic and oleic acids, with saturation of the maleic acid first, and this occurs in spite of the fact that during a separate hydrogenation oleic acid is saturated incomparably more rapidly than is maleic. In the presence of a

TABLE 2

Hydrogenation of a Mixture of Oleic and Maleic Acids in the Presence of Pd
Oleic acid 1.41 g, maleic acid 0.58 g; Pd 64 mg. Temperature of the air 18°. Pressure 721.5 mm. Theoretical absorption of hydrogen H_0 251.5 ml. $\pi_{1/2}$ −0.76 v

Absorption of H_2		Wave height	Maleic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$*	$\Delta C \cdot 10^{-5}$*	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	575	250	0	0	250	0	0
26.9	10.7	453	197	53	21.2	250	0	0
56.0	22.2	320	139	111	44.4	250	0	0
85.9	34.1	182	79	171	68.4	250	0	0
117.2	46.6	60	26	224	89.6	241	9	3.6
151.3	60.1	0	0	250	100	199	51	20.4
187.0	74.3	0	0	250	100	128	122	48.8
218.7	86.9	0	0	250	100	65	185	74.0

TABLE 3

Hydrogenation of a Mixture of Oleic and Maleic Acids in the Presence of Pt
Oleic acid 1.41 g, maleic acid 0.58 g, Pt 116 mg. Temperature of the air 16°. Pressure 716.5 mm. Theoretical absorption of hydrogen H_0 251.5 ml.

Absorption of H_2		Wave height	Maleic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	600	250	0	0	250	0	0
21.5	8.5	514	214	36	14.4	243	7	2.8
43.0	17.4	420	175	75	30.0	238	12	4.8
67.7	26.9	317	132	118	47.2	234	16	6.4
93.0	37.0	250	104	146	58.4	211	39	15.6
119.7	47.6	197	82	168	67.2	180	70	28.0
148.3	58.9	132	55	195	78.0	150	100	40.0
179.7	71.4	46	19	231	92.4	124	126	50.4
215.0	85.5	0	0	250	100	73	177	70.8
230.6	91.6	0	0	250	100	41	209	83.6

platinum catalyst both components of the mixture are saturated during the first minutes of the process; however, maleic acid is saturated at a greater rate than is oleic; therefore, the saturation of maleic acid is completed earlier than that of oleic. Thus, although not strictly maintained, in this case the process has a selective character.

3. Hydrogenation of a mixture of oleic and fumaric acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol [10] (Table 4, Fig. 3).

It is evident from Fig. 3 that the points characterizing the degree of saturation of fumaric and oleic acids, are located along the diagonal and along both its sides. Thus, it can be assumed that both acids are hydrogenated simultaneously and at the same rates, i.e., that essentially the process proceeds non-selectively.

Beginning the experiment with cinnamic acid, we should establish its polarographic behavior. Kolthoff and Lingane [11] cited the following data on this point: the reduction potential E in 1 N HCl in an aqueous medium (according to Shvaer) was −0.96 v; in 0.1 N NH_4Cl in 50% ethanol (according to Semerano and Chizini) it was −1.46 v. Heyrovsky [12] gave the reduction potential of cinnamic acid in an acid medium (pH 1.5) as −1.10, and in a neutral medium as −1.80 v. In later work [13] the same author cited the reduction potential of cinnamic acid in 0.1 N NH_4Cl in 50% ethanol as −0.78 v (with respect to the normal calomel electrode).

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* In this and in the other tables the symbol C designates concentration, and the symbol ΔC designates the decrease of concentration of each of the components of the mixture. Both values are expressed in moles/liter.

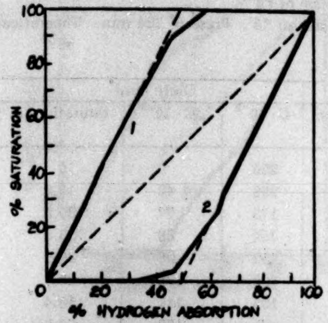


Fig. 1. Hydrogenation of a mixture of maleic and oleic acids. Catalyst palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) oleic.

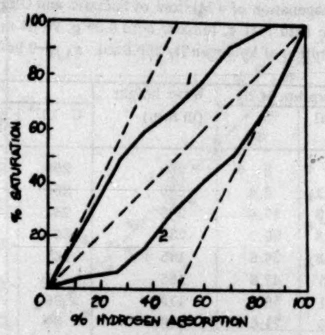


Fig. 2. Hydrogenation of a mixture of maleic and oleic acids. Catalyst-platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) oleic.

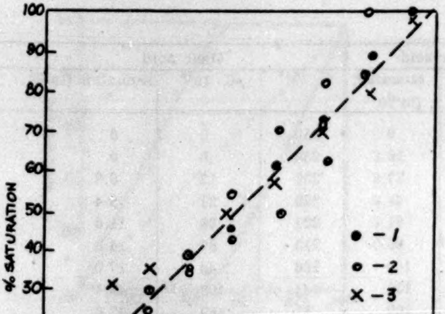


Fig. 3. Hydrogenation of a mixture of fumaric and oleic acids. Catalyst palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
1) and 2) Fumaric acid; 3) and 4) oleic acid.

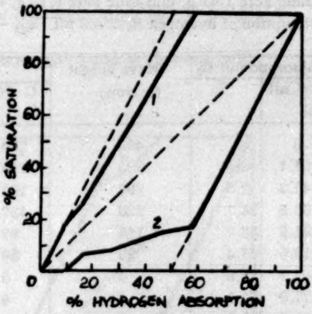


Fig. 4. Hydrogenation of a mixture of cinnamic and oleic acids. Catalyst palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) cinnamic; 2) oleic.

We carried out experiments on the polarographing of cinnamic acid in alcoholic (96%) and in alcohol-water (50%) solutions, using 0.1 N HCl or 0.1 N NH_4Cl as the inert electrolyte. In this way it was found:

1) cinnamic acid gave no polarographic waves in acidic alcoholic and in alcohol-water media;

2) a wave with a half-wave potential of −1.60 v was obtained in 0.1 N alcoholic solutions of NH_4Cl, and in alcohol-water solutions it was −1.71 v (with respect to the saturated calomel electrode);

3) there exists a strict proportionality between the diffusion current and the concentration of cinnamic acid in solution within the concentration range of $1 \cdot 10^{-5}$–$1 \cdot 10^{-3}$ mole/liter.

TABLE 4

Hydrogenation of a Mixture of Fumaric and Oleic Acids in the Presence of Pd
Oleic acid 1.41 g, fumaric acid 0.58 g, Pd 64 mg. Temperature of the air 18°. Pressure 724 mm. Theoretical absorption of hydrogen H_0 250.6 ml. $\pi_{1/2}$ −0.94 v

Absorption of H_2		Wave height	Fumaric acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	280	250	0	0	250	0	0
21.1	8.4	280	250	0	0	208	42	16.8
43.3	17.4	270	241	9	3.6	173	77	30.8
66.8	26.7	230	205	45	18.0	162	88	35.2
91.8	36.6	185	165	85	34.0	152	98	39.2
118.5	47.3	155	138	112	44.8	126	124	49.6
147.1	58.7	110	98	152	60.8	109	141	56.4
177.9	71.0	78	70	180	72.0	75	175	70.0
210.6	84.1	32	29	221	88.4	51	199	79.6
237.0	94.6	0	0	250	100	27	223	89.2
250.6	100	0	0	250	100	0	250	100

TABLE 5

Hydrogenation of a Mixture of Oleic and Cinnamic Acids in the Presence of Pd
Oleic acid 1.41 g, cinnamic acid 0.74 g, Pd 64 mg. Temperature of air 16°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 250.3 ml. $\pi_{1/2}$ −1.60 v

Absorption of H_2		Wave height	Cinnamic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	400	250	0	0	250	0	0
21.1	8.4	333	208	42	16.8	250	0	0
43.3	17.3	290	181	69	27.6	233	17	6.8
66.8	26.7	220	137	113	45.2	229	21	8.4
91.8	36.7	155	97	153	61.2	221	29	11.6
118.5	47.4	80	50	200	80.0	213	37	14.8
147.1	58.8	0	0	250	100	206	44	17.6
177.9	71.1	0	0	250	100	144	106	42.4
209.6	83.8	0	0	250	100	81	169	67.6

Employing this condition, we carried out the following experiments.

4. Hydrogenation of a mixture of oleic and cinnamic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl in 96% ethanol and the stearic acid which precipitated was filtered off (Table 5, and Fig. 4). For the present case S = 0.810 was found.

5. Hydrogenation of a mixture of oleic and cinnamic acids in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 6, and Fig. 5). S = 0.829 was found.

As is evident from these experiments, the saturation of cinnamic acid proceeds preferably, although not strictly selectively, in the presence of palladium; in the presence of platinum, saturation of oleic acid is preferable.

Further, we carried out a series of hydrogenation experiments of binary mixtures of maleic and cinnamic acids. The polarographic analysis of these mixtures was based on the fact that, in acidic alcoholic and alcohol-water solutions of cinnamic acid, as noted above, no waves are produced; under these conditions maleic acid does give a clearly expressed wave.

6. Hydrogenation of a mixture of maleic and cinnamic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol (Table 7, Fig. 6); the results of two experiments are reproduced in the figure). Here it is possible to assume that S = 0.

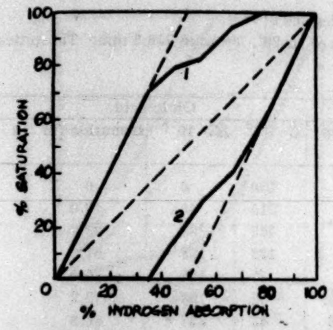


Fig. 5. Hydrogenation of a mixture of cinnamic and oleic acids. Catalyst – platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) oleic; 2) cinnamic.

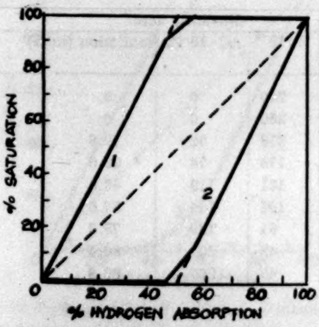


Fig. 7. Hydrogenation of a mixture of maleic and cinnamic acids. Catalyst – platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) cinnamic.

7. Hydrogenation of a mixture of maleic and cinnamic acids, in the presence of platinum.

The conditions of polarographing were the same as in the preceding experiment (Table 8, Fig. 7). S = 0.988. Similar results were obtained in a different experiment carried out at a bath temperature of 25°.

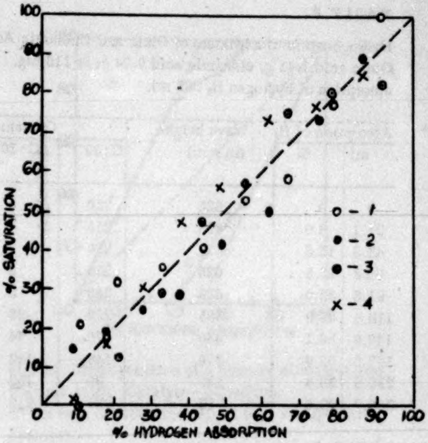


Fig. 6. Hydrogenation of a mixture of maleic and cinnamic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
1) and 2) Maleic acid; 3 and 4) cinnamic acid.

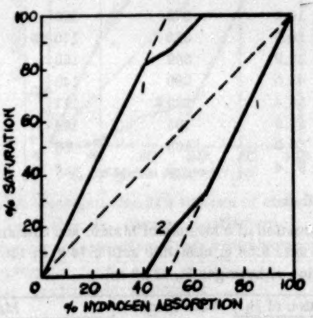


Fig. 8. Hydrogenation of a mixture of cinnamic and fumaric acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) cinnamic; 2) fumaric.

Thus, the hydrogenation of mixtures of maleic and cinnamic acids in the presence of palladium proceeds entirely non-selectively; in the presence of platinum it proceeds strictly selectively, with the saturation of maleic acid first.

TABLE 6

Hydrogenation of a Mixture of Oleic and Cinnamic Acids in the Presence of Pt
Oleic acid 1.41 g, cinnamic acid 0.74 g; Pt 116 mg. Temperature of air 28°. Pressure 716.5 mm. Theoretical absorption of hydrogen H_0 262 ml.

Absorption of H_2		Wave height (in mm)	Cinnamic acid			Oleic acid		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	625	250	0	0	250	0	0
21.1	8.0	625	250	0	0	210	40	16.0
43.3	16.5	625	250	0	0	167	83	33.2
66.8	25.5	625	250	0	0	122	128	51.2
91.8	35.0	625	250	0	0	75	175	70.0
118.5	45.2	555	222	28	11.2	52	198	79.2
147.5	56.1	440	176	74	29.6	43	207	82.8
177.9	67.9	370	148	102	40.8	12	238	95.2
210.6	80.4	245	98	152	60.8	0	250	100
243.7	93.0	88	35	215	86.0	0	250	100

TABLE 7

Hydrogenation of a Mixture of Maleic and Cinnamic Acids in the Presence of Pd
Maleic acid 0.58 g, cinnamic acid 0.74 g, Pd 64 mg. 30 ml of alcohol and 10 ml of water. Bath temperature 25°, air 20°. Pressure 725 mm. Theoretical absorption of hydrogen H_0 252 ml. $\pi_{1/2}$ −0.73 v

Absorption of H_2		Wave height (in mm)	Maleic acid			Cinnamic acid		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	470	250	0	0	250	0	0
26.3	10.4	372	198	52	20.8	250	0	0
52.6	20.9	320	170	80	32.0	218	32	12.8
82.9	32.9	300	160	90	36.0	176	74	29.6
110.9	44.0	280	149	101	40.4	131	119	47.6
139.5	55.4	220	117	133	53.2	106	144	57.6
168.9	67.0	195	104	146	58.4	61	189	75.6
199.2	79.0	105	56	194	77.6	49	201	80.4
230.4	91.4	0	0	250	100	43	207	82.8

TABLE 8

Hydrogenation of a Mixture of Maleic and Cinnamic Acids in the Presence of Pt
Maleic acid 0.58 g, cinnamic acid 0.74 g, Pt 116 mg; temperature of air 27°. Pressure 714.5 mm. Theoretical absorption of hydrogen H_0 261.8 ml.

Absorption of H_2		Wave height (in mm)	Maleic acid			Cinnamic acid		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	1012	250	0	0	250	0	0
21.4	8.2	845	209	41	16.4	250	0	0
43.3	16.5	675	167	83	33.2	250	0	0
66.8	25.5	495	122	128	51.2	250	0	0
93.0	35.5	290	72	178	79.2	250	0	0
119.7	45.7	85	21	229	91.6	250	0	0
148.3	56.6	0	0	250	100	217	33	13.2
179.1	68.4	0	0	250	100	158	92	36.8
212.4	81.1	0	0	250	100	94	156	62.4
230.6	88.1	0	0	250	100	60	190	76.0

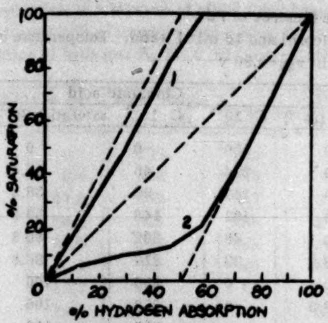


Fig. 9. Hydrogenation of a mixture of oleic and itaconic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) oleic; 2) itaconic.

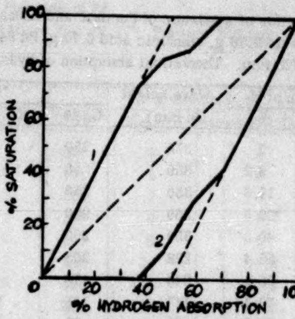


Fig. 10. Hydrogenation of a mixture of maleic and itaconic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) itaconic.

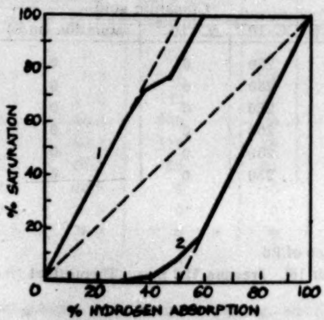


Fig. 11. Hydrogenation of a mixture of maleic and itaconic acids. Catalyst – platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) itaconic.

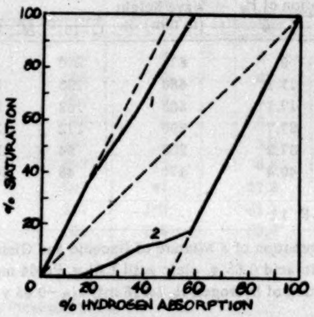


Fig. 12. Hydrogenation of a mixture of cinnamic and itaconic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) cinnamic; 2) itaconic.

8. Hydrogenation of a mixture of fumaric and cinnamic acids in the presence of palladium. For analysis, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol; under these conditions fumaric acid polarographed, but cinnamic acid did not polarograph. (Table 9, Fig. 8). For the present case S = 0.923 was found.

All the hydrogenation experiments of mixtures of fumaric and cinnamic acids in the presence of a platinum catalyst were found to be unsuccessful, in the sense that the process stopped spontaneously long before its completion. We cite the characteristics pertaining to one such experiment.

9. Hydrogenation of a mixture of fumaric and cinnamic acids in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 10).

Thus, in the presence of palladium cinnamic acid was first and almost strictly selectively hydrogenated; in the presence of platinum, as can be seen even from the uncompleted experiments, fumaric acid was saturated first.

TABLE 9

Hydrogenation of a Mixture of Fumaric and Cinnamic Acids in the Presence of Pd
Fumaric acid 0.58 g, cinnamic acid 0.74 g, Pd 64 mg, 30 ml of alcohol and 10 ml of water. Temperature of air 16°. Pressure 723 mm. Theoretical absorption of hydrogen H_0 249.2 ml. $\pi_{1/2}$ −0.90 v

Absorption of H_2		Wave height	Fumaric acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	350	250	0	0	250	0	0
23.0	9.2	350	250	0	0	204	46	18.4
48.0	19.3	350	250	0	0	154	96	38.4
73.6	29.5	350	250	0	0	102	148	59.2
100.9	40.5	350	250	0	0	48	202	80.8
130.5	52.4	288	205	45	18.0	33	217	86.8
162.6	65.3	244	174	76	30.4	0	250	100
197.8	79.4	147	105	145	58.0	0	250	100
234.9	94.3	41	29	221	88.4	0	250	100
249.4	100	0	0	250	100	0	250	100

TABLE 10

Hydrogenation of a Mixture of Fumaric and Cinnamic Acids in the Presence of Pt
Fumaric acid 0.58 g, cinnamic acid 0.74 g, Pt 116 mg. Temperature of air 27°. Pressure 713.5 mm. Theoretical absorption of hydrogen H_0 262.5 ml.

Absorption of H_2		Wave height	Fumaric acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	875	250	0	0	250	0	0
29.1	11.1	680	195	55	22.0	250	0	0
46.4	17.7	565	162	88	35.2	250	0	0
72.5	27.7	390	112	138	55.2	250	0	0
97.5	37.2	225	64	186	74.4	250	0	0
105.8	40.4	170	48	202	80.8	250	0	0

TABLE 11

Hydrogenation of a Mixture of Itaconic and Oleic Acids in the Presence of Pd
Itaconic acid 0.65 g, oleic acid 1.41 g, Pd 64 mg. Temperature of air 16°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 249.6 ml. $\pi_{1/2}$ −0.85 v

Absorption of H_2		Wave height	Itaconic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	470	500	0	0	500	0	0
21.1	8.4	450	479	21	4.2	436	64	12.8
43.3	17.3	440	468	32	6.4	359	141	28.2
66.8	26.7	430	457	43	8.6	276	224	44.8
91.8	36.7	420	447	53	10.6	186	314	62.8
118.7	47.3	410	436	64	12.8	89	411	82.2
147.6	59.0	371	395	105	21.0	0	500	100
173.4	71.3	269	286	214	42.8	0	500	100
211.7	84.7	144	153	347	69.4	0	500	100
224.5	89.8	96	102	398	79.6	0	500	100

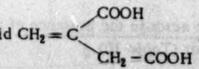
We used itaconic acid  $CH_2=C\begin{smallmatrix}COOH\\CH_2-COOH\end{smallmatrix}$ as a representative of the group of asymmetrical disubstituted ethylene derivatives, the polarographic behavior of which we studied earlier [14].

TABLE 12

Hydrogenation of a Mixture of Maleic and Itaconic Acids in the Presence of Pd

Maleic acid 0.58 g, itaconic acid 0.65 g, Pd 64 mg. Bath temperature 25°, air 17°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 251.2 ml. $\pi_{1/2}$ −1.44 v

Absorption of H_2		Wave height (in mm)	Maleic acid			Itaconic acid		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	875	500	0	0	500	0	0
21.1	8.4	728	416	84	16.8	500	0	0
43.3	17.3	572	327	173	34.6	500	0	0
66.6	26.5	411	235	265	53.0	500	0	0
91.6	36.5	236	135	365	73.0	500	0	0
118.3	47.1	145	83	417	83.4	446	54	10.8
147.4	58.7	100	57	443	88.6	356	144	28.8
178.2	71.0	0	0	500	100	290	210	42.0
205.9	82.0	0	0	500	100	180	320	64.0

TABLE 13

Hydrogenation of a Mixture of Maleic and Itaconic Acids in the Presence of Pt

Maleic Acid 0.58 g, itaconic acid 0.65 g, Pt 116 mg. Bath temperature 26°, air 26°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 253.7 ml

Absorption of H_2		Wave height (in mm)	Maleic acid			Itaconic acid		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	420	250	0	0	250	0	0
22.2	8.7	340	206	44	17.6	250	0	0
44.3	17.4	272	163	87	34.8	250	0	0
68.1	26.8	193	116	134	53.6	250	0	0
93.1	36.7	115	69	181	72.4	247	3	1.2
119.8	47.2	52	31	219	87.6	233	17	6.8
148.4	58.5	0	0	250	100	207	43	17.2
179.2	70.6	0	0	250	100	147	103	41.2
202.5	79.8	0	0	250	100	101	149	59.6

TABLE 14

Hydrogenation of a Mixture of Itaconic and Cinnamic Acids in the Presence of Pd

Itaconic acid 0.65 g, cinnamic acid 0.74 g; 64 mg Pd. Bath temperature 25°, air 17°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 250.4 ml. $\pi_{1/2}$ −0.82 v

Absorption of H_2		Wave height (in mm)	Itaconic acid			Cinnamic acid		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	190	500	0	0	500	0	0
42.5	17.0	190	500	0	0	330	170	34.0
66.7	26.6	180	474	26	5.2	260	240	48.0
92.4	36.9	170	448	52	10.4	183	317	63.4
118.9	47.5	165	434	66	13.2	91	409	81.3
146.9	58.7	157	413	87	17.4	0	500	100
175.8	70.2	113	298	202	40.4	0	500	100
206.6	82.5	67	175	325	65.0	0	500	100
209.6	83.7	62	163	337	67.4	0	500	100

10. Hydrogenation of a mixture of itaconic acid and oleic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 96% ethanol (Table 11, Fig. 9). The index of selectivity was S = 0.808.

11. Hydrogenation of a mixture of maleic and itaconic acids in the presence of palladium. For polarographing, a buffer of 25 ml of 0.2 M (H_3BO_3 + KCl), 10.65 ml of 0.2 N NaOH and 64.35 ml of water was prepared; its pH was 9.00. 1 ml of each sample was dissolved in 25 ml of the buffer. Itaconic acid produced no polarographic waves, but maleic acid also polarographed in an alkaline medium [15]. (Table 12, Fig. 10). S = 0.883 was found.

12. Hydrogenation of a mixture of maleic and itaconic acids in the presence of platinum. 1 ml of each sample was dissolved in 50 ml of buffer. In other respects the conditions of polarographing were the same as in the preceding experiment (Table 13, Fig. 11). In the present case S = 0.935.

13. Hydrogenation of a mixture of itaconic and cinnamic acids in the presence of palladium. For analysis, 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 50% ethanol. Under these conditions itaconic acid polarographed, but cinnamic acid did not (Table 14, Fig. 12). S = 0.860.

From an analysis of the experiments cited we first of all are convinced that the hypothesis proposed by Lebedev, that mixtures of ethylene derivatives of one degree of substitution are hydrogenated simultaneously, i.e., in other words, non-selectively, cannot be considered as a general principle. The nature of the saturation of binary mixtures, the degree of selectivity of saturation, fluctuates (depending on the nature of the components of the mixture and the nature of the catalyst) within wide limits – from 0 to 1. Thus, for example, in experiments which we carried out with a palladium catalyst, we found on the one hand, such pairs as maleic and cinnamic acids, or fumaric and oleic acids, which hydrogenated together at almost the same rates, and, on the other hand, such pairs as maleic and oleic acids (S = 0.97) or fumaric and cinnamic acids (S = 0.92) where one component did not react until the second was almost completely hydrogenated. Finally, we observed cases of not strictly expressed selectivity, when two components of a mixture hydrogenated simultaneously, but with sharp differences of rates; such, for example, occurs in a mixture of cinnamic and oleic acids (S = 0.81).

In the experiments with a platinum catalyst not one of the number of binary mixtures of symmetrically disubstituted ethylenes which we studied presented a picture of completely non-selective hydrogenation. Here individual pairs showed complete selectivity in the process of saturation, as, for example, maleic and cinnamic (S = 0.99) and fumaric and cinnamic acids; others showed a great or slight degree of deviation from absolute selectivity, as, for example, mixtures of cinnamic and oleic (S = 0.83) and maleic and oleic (S = 0.61) acids.

Concerning mixtures of symmetrical and asymmetrical (itaconic acid) disubstituted ethylenes, here there was always observed a more or less clear selectivity in operations with both palladium and platinum, in which in all cases the symmetrically disubstituted ethylene hydrogenated first.

SUMMARY

If all the disubstituted ethylene derivatives studied are arranged in a series, the selective designated by the symbol > and the non-selective saturations designated by the symbol =, then for the hydrogenation with palladium the series, maleic acid = cinnamic acid > oleic acid = fumaric acid > itaconic acid is obtained, and for hydrogenation with platinum the series, maleic acid > fumaric acid > cinnamic acid > oleic acid > itaconic acid, is obtained.

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GRIGNARD-WÜRTZ REACTIONS WITH β- AND γ-ALKYNYL HALIDES

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In a number of instances it has been shown by different investigators [1-3] that condensation of allyl types of halides with both tertiary and primary alkylmagnesium halides proceeds with high yields, and may serve as a convenient method for the synthesis of various olefins, and also – as a result of hydrogenation – the paraffin hydrocarbons. The reaction, of course, considering the allyl rearrangement mechanism, can also be used for allyl type halides which are capable of isomerizing, but here it is necessary to carry out the reaction in a larger volume, keeping in mind the fractionation for the purposes of removal of the isomer which is present as an admixture, and the lowered yields of the branched halides [4].

Whereas the introduction of a multiple bond in the β-position makes the halide considerably more active, compared with the alkyl halide of the same structure, and in a number of cases (for branched halides) enables us also to carry out reactions which do not occur at all in the absence of a multiple bond, the presence of a double bond in the α- and γ-positions, on the other hand, reduces the activity of the halides almost to zero [5]. Likewise, both tertiary and secondary and primary halides with a double bond in the γ-position were shown to be inactive. There are some investigations in the literature devoted exclusively to the condensation reaction of alkynylmagnesium halides with tertiary alkynyl halides with a triple bond in the β-position [6]. In these investigations were noted both the high yield specified by the triple bond, and also the presence of acetylene-allene-diene rearrangements, the extent of which depends on the nature of the halohydrin of the acetylene alcohol and on the nature of the Grignard reagent.

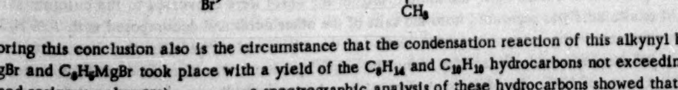
The study of the behavior in condensation reactions of primary alkynyl halides with a triple bond in both the β- and γ-positions was the problem of the present work. We planned for investigation the condensation of

$$C_2H_5MgBr \text{ with } CH_3-C\equiv C-CH_2Br \text{ (I) and with } CH_3-C\equiv C-CH_2-CH_2Br. \text{ (II)}$$

We were able to obtain the first bromide relatively easily. In the synthesis of the alcohol corresponding to the second halide, according to Iotsich's method [7], ethylenebromohydrin which was characterized by the same boiling point and d_4^{20} 1.7720, was obtained instead of the alcohol. Apparently, this alcohol was not obtained by Iotsich either, who for its characteristics was limited to the citation of its boiling point. We were able to obtain this alcohol, having d_4^{20} 0.9002, by condensation of ethylene oxide with Na-methylacetylene, but for study of the Grignard-Würtz reaction we preferred to use the more readily available bromohydrin of its analog $C_4H_9-C\equiv C-CH_2-CH_2Br$ (III). As also with its olefin analog, condensation of the halide (III) with C_2H_5MgBr did not take place at all. The condensation of the halide (I) went according to the scheme:

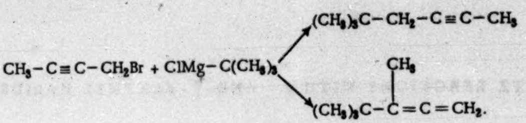
$$\underset{\text{(I)}}{CH_3-C\equiv C-CH_2Br} + C_2H_5MgBr \rightarrow CH_3-C\equiv C-CH_2-C_2H_5 + CH_3-C\equiv C-CH_2-CH_2-C\equiv C-CH_3.$$

The smaller yield of the acetylene hydrocarbon (25%) instead of the 50% yield noted in the condensation of the tertiary acetylenyl halide, and the formation of octadiyne-2,6 was characteristic of the reactions. All this indicates the lower rate of condensation of the primary acetylene β-halide compared with the tertiary. We were unable to detect an allene-diene rearrangement here; however, it is possible that it occurred partially, but that the isoprene homolog which formed was converted to a resinous polymer.



$$CH_3-C\equiv C-CH_2Br \rightarrow \overset{CH_3}{\underset{Br}{>}}C=C=CH_2 \rightarrow C_2H_5-\underset{CH_3}{\underset{|}{C}}=C=CH_2 \rightarrow CH_2=\overset{C_2H_5}{\overset{|}{C}}-CH=CH_2.$$

Favoring this conclusion also is the circumstance that the condensation reaction of this alkynyl halide with $(CH_3)_3CMgBr$ and C_6H_5MgBr took place with a yield of the C_8H_{14} and $C_{10}H_{10}$ hydrocarbons not exceeding 10% (all the rest produced resinous polymers), a spectrographic analysis of these hydrocarbons showed that they, in addition to triple bonds, contained conjugated double bonds. This latter circumstance induced us to repeat the synthesis and to carry out an ozonization of the synthesis products, which showed that the reaction proceeds here according to the scheme:



$$CH_3-C\equiv C-CH_2Br + ClMg-C(CH_3)_3 \rightarrow \begin{cases} (CH_3)_3C-CH_2-C\equiv C-CH_3 \\ (CH_3)_3C-\overset{CH_3}{\overset{|}{C}}=C=CH_2. \end{cases}$$

EXPERIMENTAL

1. Reaction of 1-bromobutyne-2 (I) with C_2H_5MgBr. Butyn-2-ol-1 was obtained from 1,3-dichlorobutene-2 by saponification, according to Tishchenko [8], followed by the splitting off of HCl, according to Mkryan [9]; 1-bromobutyne-2 was obtained under the conditions of [10]. 3 g of dry pyridine was added to 50 g of butyn-2-ol-1 dissolved in 150 ml of dry ether, and 80 g of PBr_3 in 40 ml of ether was added dropwise. 48 g (50%) of 1-bromobutyne-2 was obtained:

B.p. 40-41° at 19mm, n_D^{20} 1.5090, d_4^{20} 1.5191, MR_D 26.12, calc. 26.36.
Found %: C 36.08, 35.82; H 3.35, 3.49; Br 60.57, 60.85. C_4H_5Br. Calculated %: C 36.09; H 3.7; Br 60.05.

30 g of 1-bromobutyne-2 in 50 ml of ether was added dropwise to ethylmagnesium bromide, prepared from 7 g of magnesium, 30 g of C_2H_5Br and 100 ml of ether. A strong evolution of heat was observed on addition of the acetylene bromide. After a 4-hour stirring at the boiling point of ether, the product was decomposed, washed and dried. 2 fractions were obtained: 1st, 79-85°, 5 g (25%); 2nd, 80-85° at 45 mm, 8 g; and a residue of 3 g, a resinous product.

The 1st fraction was hexyne-2: n_D^{20} 1.4121, d_4^{20} 0.7465. The Raman* spectrum showed the presence of the frequencies 2240, 2234 and 2303 cm^{-1}, which corresponded to hexyne-2. By hydration a ketone was obtained, the semicarbazone of which melted at 120°, which corresponded to the melting point of the semicarbazone of methyl butyl ketone.

The 2nd fraction was octadiyne-2,6:

n_D^{20} 1.4740, d_4^{20} 0.8414, MR_D 35.40; calc. 35.01.
Literature values [11]: B.p. 62° at 19 mm, n_D^{30} 0.828, d_4^{30} 1.4658.

The absorption spectrum in the infrared region showed the presence of the following bands (up to 7 μ): 3.4, 4.58 and 6.07 μ. On the basis of the fact that the band corresponding to the $C\equiv C$ bond had a large intensity, it followed that the $C\equiv C$ bond was not located in the middle of the molecule.

On conducting of an experiment in the reverse order, i.e., by addition of ethyl bromide to the butynylmagnesium bromide, no C_6H_{10} fraction, but only octadiyne-2,6, formed. By the Raman method the latter showed the presence of both triple and double bonds.

2. Reaction of 1-bromobutyne-2 (I) with tert.-C_4H_9MgCl. 50 g of 1-bromobutyne-2 was added to tert.-C_4H_9MgCl, prepared from 12 g of magnesium and 55 g of tert.-C_4H_9Cl in 200 ml of ether. A violent boiling was observed on addition of the C_4H_5Br. The reaction was carried out under the same conditions as was the preceding synthesis. 5 g (10%) of the hydrocarbon was obtained:

B.p. 38-42° at 25 mm, n_D^{20} 1.4302, d_4^{20} 0.7923 and a resinous product.
Found %: C 86.52, 86.11; H 11.82, 11.93. C_8H_{14}. Calculated %: C 87.26; H 12.73.

The taking of a Raman spectrum showed the presence of the frequencies 2236(4), 2299(5), 3060, 1605 (b), 1638(5), 1026(5), which indicated the presence of compounds with double and triple bonds.

4.5 g of the hydrocarbon was ozonized. Among the acid ozonization products we were able to identify formic acid by the calomel method, and acetic acid by the cacodyl test. The tert.-butylacetic acid was lost. In order to demonstrate the presence of oxalic acid, the sodium salts of the acids were converted to the calcium salts. The calcium salt of oxalic acid was separated from the salts of the other acids and decomposed with 10% H_2SO_4; the oxalic acid was extracted with ether. After evaporation of the ether, and recrystallization from water, oxalic acid with a m. p. of 99° was separated. Pinacoline, from the neutral products, was identified as the 2,4-dinitrophenylhydrazone with a m. p. of 124°. An addition product with maleic anhydride was obtained, which we were unable to separate in pure form by recrystallization. Thus, the resulting hydrocarbon was a mixture of acetylene, allene, and possibly diene hydrocarbons.

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* Combination light scattering.

3. Reaction of 1-bromobutyne-2 (I) with C_6H_5MgBr. 45 g of 1-bromobutyne-2 was added dropwise to phenylmagnesium bromide, prepared from 11 g of Mg, 150 ml of ether and 60 g of C_6H_5Br. The reaction was carried out under conditions similar to those of the first synthesis. 10 g of the original acetylene bromide and 12 g of the hydrocarbon with a b.p. of 70-82° at 13 mm were obtained:

n_D^{20} 1.5346, d_4^{20} 0.9658, MR_D 41.89; calc. 42.76.
Found %: C 91.52, 91.81; H 7.62, 7.58; $C_{10}H_{10}$. Calculated %: C 92.30; H 7.72.

Investigation of the resulting compounds by the Raman method showed the presence of the following frequencies: 186(1), 619(4), 812(2), 922(2), 1002(8), 1027(5), 1605 (5b), 1638(3), 2237(5), 2294(4) and 3060(5), which indicated the presence of a monosubstituted aromatic ring, and a double and triple bond in the molecules. We were unable to obtain the addition compound with maleic anhydride; a resin separated.

4. Reaction of 1-bromoctyne-3 (III) with RMgX. Octyn-3-ol-1 was prepared by method [12] from sodium hexynide and ethylene oxide in liquid ammonia. The yield was 40% based on the hexyne which reacted. The b.p. was 106° at 92 mm, n_D^{20} 1.4540. The 3,5-dinitrobenzoate of octyn-3-ol-1 had a m. p. of 45°.

Found %: N 8.85, 8.87. $C_{15}H_{16}O_6N_2$. Calculated %: N 8.75.

1-Bromoctyne-3 was obtained under the conditions specified in the literature [10]. 20 g (55%) of 1-bromoctyne-3 was obtained from 25 g of octyn-3-ol-1 in ether and pyridine, and 25 g of PBr_3:

B. p. 90-93° at 22 mm, n_D^{20} 1.4650, d_4^{20} 1.1387, MR_D 45.66; calc. 44.84.
Found %: Br 40.82, 41.42. $C_8H_{13}Br$. Calculated %: Br 42.32.

40 g of 1-bromoctyne-3 was added to ethylmagnesium bromide, prepared from 6 g of magnesium and 38 g of C_2H_5Br in 150 ml of ether. No evolution of heat from the reaction substance was observed. The temperature of the reaction substance was brought to 35°, and the mixture was boiled for 12 hours, after which the product was treated by the usual method. The original acetylene bromide was recovered.

5. Preparation of the Grignard reagent from 1-bromobutyne-3. By preparation of the original product of butyn-3-ol-1 by method [12], we obtained, together with the alcohol, the 3-butynoic ether of ethylene glycol (not mentioned in [12]). 30 g (42%) of butyn-3-ol-1 and 5 g of the 3-butynoic ether of ethylene glycol were obtained from 24 g of sodium, 700 ml of ammonia, acetylene, and 55 g of ethylene oxide. The 3,5-dinitrobenzoate of butyn-3-ol-1, m. p. 112°, was obtained with α-naphthylamine.

Found %: C 61.25, 60.98; H 4.38, 4.49. $C_{21}H_{17}O_6N_3$. Calculated %: C 61.90; H 4.17.

The 3-butynoic ether of ethylene glycol had:

B. p. 80° at 12 mm, n_D^{20} 1.4525, d_4^{20} 0.9939, MR_D 30.97; calc. 31.06.
Found %: C 63.38, 63.13; H 8.94, 9.03. $C_6H_{10}O_2$. Calculated %: C 63.15; H 8.85.

The substance gave a white precipitate with $AgNO_3$. The 3,5-dinitrobenzoate of the 3-butynoic ether of ethylene glycol had a m. p. of 52°.

Found %: C 50.75, 50.65; H 4.05, 4.15; N 9.85. $C_{13}H_{12}O_7N_2$. Calculated %: C 50.14; H 3.82; N 9.91.

The 3,5-dinitrobenzoate of the 3-butynoic ether of ethylene glycol with α-naphthylamine had a m. p. of 75°.

Found %: C 61.20, 61.40; H 4.64, 4.84. $C_{23}H_{21}O_7N_3$. Calculated %: C 60.81; H 4.65.

Depending on the order of addition of the reagents, we obtained the sulfite of butyn-3-ol-1 and 1-chlorobutyne-3.

The sulfite of butyn-3-ol-1. $(HC\equiv C-CH_2-CH_2O)_2SO$. 35 g of thionyl chloride was added dropwise during 1 hour to 10 g of butyn-3-ol-1, 30 g of pyridine, and 30 ml of dry ether at 0°. After addition of the $SOCl_2$ the temperature was brought to room temperature, and stirring was continued for 3 hours, after which ice water at 0° was added. The product was extracted with ether, neutralized with soda and dried with $CaCl_2$. 5 g (39%) of the sulfite was obtained.

B. p. 120° at 10 mm, n_D^{20} 1.4750, d_4^{20} 1.1341, MR_D 46.16; calc. 46.27.
Found %: S 17.28, 16.90; C 51.80, 51.87; H 5.52, 5.38. $C_8H_{10}O_3S$. Calculated %: S 17.20; C 51.61; H 5.30.

1-Chloro-butyne-3 was obtained by a reverse addition of the reagents, i. e., the acetylene alcohol in pyridine was added to thionyl chloride dissolved in ether. From 16 g of butyn-3-ol-1 in 16 g of pyridine, and 35 g of thionyl chloride in 30 ml of ether, 8 g (38%) of 1-chloro-butyne-3 was obtained:

B. p. 33-34° at 25 mm, n_D^{20} 1.4402.
Literature values [13]: B. p. 86° at 762 mm, n_D^{20} 1.4382.

The 1-chloro-butyne-3 did not react with magnesium.

An organomagnesium compound was obtained from 2 g of magnesium and 20 g of bromo-1-butyne-3 by addition of $HgCl_2$ in ether. A current of CO_2 was passed into the organomagnesium compound. After the usual treatment, and after removal of the ether, 3 g of a resinous product remained in the flask. From the resinous product, by extraction with petroleum ether, white crystals of pentynoic acid $HC\equiv C-CH_2-CH_2-COOH$ with a m. p. of 53°, obtained earlier by another method (from the dibromide) [14], were separated.

Pentyn-3-ol-1 An attempt to obtaine pentyn-3-ol-1, according to Iotsich, from methylacetylenemagnesium bromide and ethylene oxide was unsuccessful. On carrying out the reaction at an increased temperature (38-40°), decomposition with evolution of a brown, corrosive smoke was observed. We were able to obtain pentyn-3-ol-1 only from sodium methylacetylenide and ethylene oxide in liquid ammonia. The yield was 23%:

B. p. 34° at 9 mm, n_D^{20} 1.4450, d_4^{20} 0.9002, MR_D 24.82; calc. 24.81.
Phenylurethan: acicular crystals with m. p. 77°.
Found %: N 6.91, 7.04. $C_{12}H_{13}O_2N$. Calculated %: N 6.89.
3,5-Dinitrobenzoate m. p. 86°.
Found %: C 52.30; H 3.98; N 10.10. $C_{12}H_{10}O_6N_2$. Calculated %: C 51.79; H 3.60; N 10.07.

The optical investigations were made by Yu. P. Egorov.

SUMMARY

1. It was shown that a mixture of acetylenic and dienic hydrocarbons is formed by reaction of a primary alkynyl halide, which contains the triple bond in the β-position, with RMgX [where R = C_2H_5, $(CH_3)C$, and C_6H_5].

2. It was shown that, similar to the halohydrins of the olefin series, a holohydrin which contains the triple bond is the γ-position did not condense with RMgX.

3. Pentyn-3-ol-1, its derivatives and a series of derivatives of other acetylenic alcohols were obtained for the first time.

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CONTACT TRANSFORMATIONS OF PROPYLCYCLOHEPTANE IN THE PRESENCE OF PLATINIZED CARBON

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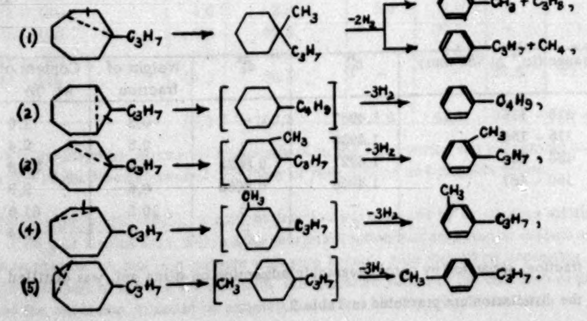
In previous investigations [1] we showed that, on passing the simplest alkyl- and arylcycloheptane hydrocarbons over platinized carbon under the conditions of dehydrogenation catalysis, isomerization of the seven-membered ring to a six-membered ring took place with the formation of considerable quantities of gem-dialkylsubstituted cyclohexane hydrocarbons. For example, methylcycloheptane contacted at 320° with platinized carbon, together with the formation of aromatic hydrocarbons (toluene, ethylbenzene, m-, p- and o-xylols), gave about 17% of gem-dimethylcyclohexane. Under similar experimental conditions ethylcycloheptane gave about 11% of gem-methylethylcyclohexane, and also a mixture of aromatic hydrocarbons consisting of ethylbenzene, and m-, o- and p-methylethylbenzenes. Phenylcycloheptane, under the same experimental conditions, gave about 7% gem-methylphenylcyclohexane and also a complex mixture of aromatic hydrocarbons.

It was of interest to study the phenomenon of contact isomerization of hydrocarbons of the cycloheptane series, which we observed, for propylcycloheptane. The propylcycloheptane which we synthesized was contacted with 10% activated carbon at 320°. The liquid portion of the catalyzate, in order to separate the naphthenic hydrocarbons from the aromatic hydrocarbons, was subjected to a chromatographic adsorption on silica gel. The naphthenic fraction, separated as a result of the chromatographic adsorption, consisted of gem-methylpropylcyclohexane. The aromatic fraction obtained by chromatographic adsorption was distilled from a column having an efficiency of 40 theoretical plates. The composition of the aromatic hydrocarbon fraction was established both by chemical methods and by a study of the Raman spectra.

On the basis of the results of the investigation, the approximate proportion of hydrocarbons in the total catalyzate of the contact transformation of propylcycloheptane (in %) was as follows: gem-methylpropylcyclohexane about 28, propylbenzene about 30, o-methylpropylbenzene about 20, m-methylpropylbenzene about 9, p-methylpropylbenzene about 8, butylbenzene about 4, and toluene about 1.

The directions of the contact transformation reactions of propylcycloheptane, under the experimental conditions which we selected, were analogous to those of the transformations of the alkylcycloheptanes which we studied earlier, and can be expressed by the following reaction scheme:



The presence of propylbenzene and toluene in the contact transformation reaction products of propylcycloheptane, to a high degree of probability can be accounted for by the occurrence of a secondary process – the catalytic transformation of gem-methylpropylcyclohexane (1). Earlier we observed a similar phenomenon of catalytic cleavage of the methyl group, encountered in the gem-methylalkylcyclohexanes during a study of the behavior of these hydrocarbons in reactions over platinized carbon, under the conditions of dehydrogenation catalysis [2].

EXPERIMENTAL

Synthesis of Propylcycloheptane

1-Propylcycloheptanol-1 was obtained from suberone and propylmagnesium bromide. This alcohol was dehydrated in the presence of iodine, and moreover, the 1-propylcycloheptene-1 which was obtained was hydrogenated to propylcycloheptane over platinized carbon at room temperature. After a vacuum distillation the propylcycloheptane had the following constants:

B. p. 181.4° (750 mm), 61.0° (9 mm), n_D^{20} 1.4500, d_4^{20} 0.8178, MR_D 46.01; calc. 46.18.
6.445 mg sub.: 20.248 mg CO_2; 8.348 mg H_2O. 6.160 mg sub.: 19.320 mg CO_2; 7.950 mg H_2O.
Found %: C 85.74, 85.60; H 14.49, 14.44. $C_{10}H_{20}$. Calculated %: C 85.63; H 14.37.

The yield of propylcycloheptane was 31.6% of the theoretical, based on suberone.

Literature values [3]: B. p. 183-184° (756 mm), n_D^{18} 1.4502, d_4^{18} 0.8175.

Contact Transformations of Propylcycloheptane

60 ml of 10% platinized carbon was placed in a catalytic tube, and 35 g of propylcycloheptane was passed over the catalyst (without a gas-carrier) at 320° at a volume rate of 0.2.

The results of the experiments are cited in Table 1.

TABLE 1

Experiment No.	n_D^{20} of catalyzate	Quantity of gas evolved (in liters)	Weight of catalyzate obtained (in g)
1	1.4680	9.78	31.2
2	1.4770	4.55	30.3
3	1.4805	3.31	29.7
4	1.4840	3.15	29.5

The gaseous products of the catalysis were analyzed in a VTI apparatus. The results of the gas analysis (in %) were: H_2 90.3; C_nH_{2n+2} 9.1.

Investigation of the catalyzate. In order to separate the naphthenic hydrocarbons from the aromatic hydrocarbons which formed during catalysis, the catalyzate obtained by the contact transformations of propylcycloheptane was subjected to a chromatographic adsorption on silica gel. The naphthenic fraction (8.5 g) isolated by this method of separation boiled at 172-174° (757 mm) and had n_D^{20} 1.4888, d_4^{20} 0.8089. A comparison of the constants of the resulting fraction with those of the gem-methylpropylcyclohexane which we synthesized earlier [4], enabled us to assume that it consisted chiefly of gem-methylpropylcyclohexane. The constants of the gem-methylpropylcyclohexane which we synthesized were as follows: b. p. 174.0-174.5° (759 mm), n_D^{20} 1.4445, d_4^{20} 0.8077.

TABLE 2

Fractions	Boiling range (in ° at 752 mm)	n_D^{20}	d_4^{20}	Weight of fraction	Content of fractions (in wt. %)
1	110 - 115	1.4967	–	0.2	1.0
2	115 - 156	1.4930	–	0.5	2.4
3	156 - 160	1.4921	0.8625	7.5	36.8
4	160 - 181	1.4956	0.8652	0.6	2.9
Residue		–	–	10.5	51.5
Losses		–	–	1.1	5.4

The aromatic fraction, separated by chromatographic adsorption on silica gel, was distilled.

The results of the distillation are presented in Table 2.

On distillation of the residue (10.5 g) from a small flask, a 5th fraction, which boiled in the range of 181-185° (758 mm), n_D^{20} 1.5011, d_4^{20} 0.8713, was obtained in a quantity of 10.3 g. We used both a chemical method of investigation, and the Raman method of investigation, in order to establish the composition of the individual fractions of the catalyzate of propylcycloheptane.

a) Optical investigation of the catalyzate. Literature values for the spectrum of n-propylbenzene [5], and for the isomeric o-, m- and p-methylpropylbenzenes [6], and also for the spectrum of gem-methylpropylcyclohexane, which we studied earlier [4], were used for interpretation of the Raman spectra of the catalyzate. The dearomatized portion of the catalyzate, and also the 3rd fraction and 5th fraction (obtained by fractionation of the residue) of the aromatic portion of the catalyzate, was subjected to an optical investigation.

The spectrum of the dearomatized portion of the catalyzate was shown to be identical with that of gem-methylpropylcyclohexane. The presence of propylcycloheptane in it was not detected.

The 3rd fraction (b. p. 156-160°) of the aromatic portion of the catalyzate contained chiefly propylbenzene, which was identified by a complete set of frequencies.

The 5th fraction (b.p. 181-184°) contained 1-methyl-2-propylbenzene, 1-methyl-3-propylbenzene and 1-methyl-4-propylbenzene, the presence of which was established by a set of analytically significant frequencies.

Using data on the line intensities in the spectra of the individual hydrocarbons [6] and data on the blackening of the analytical lines in the spectrum of the fraction, we were able to make an approximate determination of the quantitative composition of the 5th fraction. Calculation showed that it had the following composition (in %): 1-methyl-2-propylbenzene about 48, 1-methyl-3-propylbenzene about 25, 1-methyl-4-propylbenzene about 22.

Moreover, in the 5th fraction, obviously butylbenzene was present (there were lines of this hydrocarbon superimposed with lines of the other components of the fraction; however, there was also a non-superimposed line of 621 cm^{-1}, which most likely belonged to butylbenzene).

b) Chemical investigation of the catalyzate. The 1st fraction (b. p. 110-115°), as its constants showed, consisted chiefly of toluene. On nitration of this fraction, a nitro product was obtained which after recrystallization from ethanol had a m. p. of 69-70°. A test of a mixture with 2,4-dinitrotoluene gave no melting point depression.

The 2nd fraction (b. p. 115-156°), because of its wide boiling range and because of its small quantity, was not studied.

TABLE 3

Fractions	Boiling range at 752 mm	Quantity		Per cent content					
		(in g)	in percentages of total quantity of aromatics	toluene	propylbenzene	methylpropylbenzene			butylbenzene
						ortho	meta	para	
1	110 - 115°	0.2	1.0	1.0	–	–	–	–	–
2	115 - 156*	0.5	2.6	0.6	2.0	–	–	–	–
3	156 - 160	7.5	39.3	–	39.3	–	–	–	–
4	160 - 181	0.6	3.1	–	0.3	1.3	0.7	0.5	0.3
5	181 - 185	10.3	54.0	–	–	25.6	11.7	10.8	5.3
		19.1	100.0	1.6	41.6	27.5	12.4	11.3	5.6

* The approximate quantitative content of hydrocarbons in the 2nd fraction was calculated on the basis of the indices of refraction of the fraction studied and those of pure toluene and propylbenzene.

The 3rd fraction (b. p. 156-160°). 2 g of the fraction was oxidized by an aqueous solution of potassium permanganate [7]. 1.88 g of a solid acid, which after recrystallization and sublimation melted at 120°, was obtained as a result of the oxidation. A test of a mixture with pure benzoic acid showed no depression. On the basis of a comparison of the constants of the 3rd fraction with the literature values of the constants of propylbenzene and with the results of the oxidation, it could be assumed that it was chiefly propylbenzene.

The literature values for propylbenzene [5] are: b.p. 159.2° (751 mm), n_D^{20} 1.4919, d_4^{20} 0.8626.

The 4th fraction (b. p. 160-181°). In the oxidation products of 0.6 g of the fraction the following acids were obtained: benzoic (0.05 g), orthophthalic (0.13 g), isophthalic (0.08 g), and terephthalic (0.05 g). The formation of the acids could be attributed to the oxidation of propylbenzene, and o-, m- and p-methylpropylbenzenes.

The 5th fraction (b. p. 181-185°). On oxidation of 5.0 g of the fraction, the following acids were separated: benzoic (0.18 g), orthophthalic (1.21 g), isophthalic (0.53 g), and terephthalic (0.50 g).

The presence of benzoic acid in the oxidation products of the 5th fraction is accounted for, apparently, by the oxidation of butylbenzene, but not propylbenzene, since the boiling point of the latter (159.2°) is low for the boiling range of the 5th fraction. The formation of the phthalic acids should be attributed to the oxidation of o-, m- and p-methylpropylbenzenes.

The composition of the fractions was calculated (Table 3) on the basis of the physical constants of the individual fractions obtained by fractionation of the aromatic portion of the catalyzate of propylcycloheptane, and on the basis of the chemical investigation which we employed.

SUMMARY

The contact transformations of propylcycloheptane, in the presence of platinized carbon at 320°, was studied, and it was found that the transformations take place with the formation of considerable quantities of 1-methyl-1-propylcyclohexane and a mixture of aromatic hydrocarbons, consisting of toluene, propylbenzene, butylbenzene, o-, m- and p-methylpropylbenzenes.

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CATALYTIC PRODUCTION OF MIXED KETONES FROM PRIMARY ALCOHOLS

III. KETONIZATION OF A MIXTURE OF n-BUTYL AND ISOAMYL ALCOHOLS

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Processes of the formation of mixed ketones by passing mixtures of primary alcohols, ethyl and n-butyl and ethyl and isoamyl, over a copper activated catalyst were described in previous reports [1, 2]. Further investigations provided a new confirmation of the applicability of these processes to other systems. Unlike the two systems studied, a mixture of butyl and isoamyl alcohols is characterized by an increase of the molecular weights of the alcohols and by the absence of ethyl alcohol, which, as already mentioned, itself has the capacity to form mixed ketones and acetone. As will be obvious below, propyl isobutyl ketone, in a yield of 25-30% of the theoretical, was obtained by ketonization of a mixture of butyl and isoamyl alcohols.

It can be concluded from an examination of the results of experiments with mixtures of butyl and isoamyl alcohols, in molar ratios of 1 : 1, 1 : 2, 2 : 1 and 3 : 1, at temperatures from 275 to 425°, and at a constant volume rate (150), that the highest yields of propyl isobutyl ketone are obtained at a temperature of 350-375° (Table 1). The optimum ratios of alcohols in the mixture proved to be the molar ratios of 2 : 1 and 3 : 1. The ester yields, reaching a maximum at 275-300°, decreased continuously with a further increase of the temperature.

TABLE 1

Temperature of experiments	Yields of products (in % of the original mixture of alcohols)						
	dipropyl ketone	propyl isobutyl ketone	diisobutyl ketone	aldehydes	esters	butyl alcohol	isoamyl alcohol
			Molar ratio 1 : 1				
275*	0.6	0.6	1.2	7.2	54.5	9.0	18.9
300	1.6	1.2	1.6	7.3	50.8	7.2	14.1
325	5.0	4.8	1.0	13.1	37.5	5.7	5.6
350	6.3	6.2	2.4	14.3	23.6	2.3	7.4
375	6.4	8.4	3.9	25.0	19.0	3.4	6.3
400	4.5	6.7	1.4	24.2	7.3	3.5	17.0
425	3.4	7.4	5.0	9.7	6.6	5.6	12.8
			Molar ratio 1 : 2				
275	0.0	1.9	0.0	3.0	41.6	6.9	24.8
300	0.0	2.7	0.0	5.8	50.5	6.2	18.0
325	1.1	4.3	0.0	6.4	45.5	3.5	14.5
350	10.8	0.9	0.0	18.0	30.5	5.3	8.0
375	4.0	7.9	2.0	17.0	16.2	2.0	7.5
400	13.1	5.1	5.1	9.9	11.9	1.5	6.2
425	0.9	2.3	27.0	12.7	11.8	4.3	10.7
			Molar ratio 2 : 1				
275	0.2	2.3	0.0	3.2	46.6	22.5	14.0
300	4.3	2.7	0.0	11.0	58.1	12.2	10.5
325	5.3	5.1	3.0	10.2	45.9	8.0	1.8
350	8.5	10.4	5.3	10.9	36.0	7.9	0.0
375	13.7	8.4	2.4	10.8	17.8	8.8	0.0
400	3.8	9.5	4.0	18.5	12.1	15.2	0.0
425	4.4	8.7	1.5	12.6	9.7	18.0	11.4
			Molar ratio 3 : 1				
350	26.6	3.6	0.0	8.4	11.2	2.8	5.6
375	22.0	15.6	2.6	10.2	7.3	0.0	4.0

At 350-375° a maximum was approached for mixed and symmetrical ketones.

Unlike the preceding systems, the aldehydes had a maximum at 375-400°, i. e., close to the maximum for ketones. The ester yields at the temperatures optimum for ketonization were always large (about 36%). In this case, apparently, the stage of ketonic decomposition of esters is the inhibiting stage in the formation of ketones. At high temperatures (375-400°) the decomposition of esters with the formation of aldehydes is likely. Also unlike the preceding systems, considerable quantities of a symmetrical ketone (dipropyl ketone) corresponding to the low-molecular alcohol, together with the mixed ketone, are formed during the ketonization.

TABLE 2

Volume rate	Yields of products (in % of the original mixture of alcohols)						
	dipropyl ketone	propyl-isobutyl ketone	diisobutyl ketone	aldehydes	esters	butyl alcohol	isoamyl alcohol
52	24.9	5.0	3.5	6.0	10.2	6.0	8.3
100	33.5	10.2	1.0	5.2	4.3	3.2	4.7
150	22.0	15.6	2.6	10.2	7.3	0.0	4.0
202	2.3	2.9	0.6	16.2	13.7	26.2	15.8

TABLE 3

Experimental conditions	Yields of products (in % of original mixture of alcohols)					
	dipropyl ketone	propyl isobutyl ketone	diisobutyl ketone	aldehydes	esters	butyl and isoamyl alcohols
in the presence of hydrogen	22.0	15.6	2.6	10.2	7.3	4.0
without hydrogen (1st hour)	23.0	4.6	0.0	10.6	8.6	7.6
without hydrogen (2nd hour)	15.6	4.5	3.0	12.5	8.8	17.0

A study of the effect of volume rate was carried out under optimum conditions (molar ratio of mixture 3 : 1, temperature 375°). The volume rate was varied from 50 to 200. It is evident from the data of Table 2 that the yields of propyl isobutyl ketone increased with an increase of the volume rate from 50 to 150, but decreased sharply with a further increase to 200. Decrease of the contact time brought about an increase of the yields of aldehydes and esters. A comparison of the ketone yields, on the one hand, and that of the aldehydes and esters, on the other, serves to verify the hypothesis of the intermediate formation of aldehydes and esters during ketonization.

In order to study the effect of hydrogen, a mixture of alcohols in a molar ratio of 3 : 1 was passed over the catalyst at 375° without simultaneous passage of hydrogen. From the data of Table 3 it follows that in the absence of hydrogen the yields of propyl isobutyl ketone were sharply reduced, the yields of aldehydes and esters increased simultaneously, and the quantities of unreacted original alcohols increased.

We also investigated two mixtures with participation of methyl alcohol (methyl-ethyl, methyl and n-butyl alcohols). Experiments with the first mixture were carried out at alcohol molar ratios of 1 : 1 and 1 : 2 and at temperatures from 275 to 325°. Experiments with the second mixture were carried out at the same alcohol ratios and at temperatures from 275 to 375°. The experiments, a detailed description of which is not cited, showed that under the conditions indicated, partial or complete decomposition of the methyl alcohol to CO and H_2 occurs and low yields of the liquid products were obtained. No mixed ketones were formed. Thus, mixtures of methyl alcohol with other primary alcohols were unsuitable for carrying out the ketonization reaction (at least at ordinary pressure).

Examining schemes of consecutive transformations of primary alcohols to ketones which are known in the literature [1], with consideration of our experimental data obtained in the ketonization investigation of binary mixtures of primary alcohols, it should be noted that Klyukvin and Ipatyev's aldol mechanism proved to be inapplicable to this process. Neither aldols nor the corresponding secondary alcohols, assumed to be intermediate products of the aldol scheme, were found in a single instance in the reaction products.

The available facts indicated the use of the ester scheme of Sabatier-Kagan, Sobolev and Lyubarsky. Considerable quantities of esters were invariably observed in the reaction products at low temperatures. For a mixture of ethyl and isoamyl alcohols, all four of the esters the formation of which could be assumed by the ester scheme, the ethyl and isoamyl esters of isovaleric acid, the ethyl and isoamyl esters of acetic acid, were separated and identified. In experiments with other mixtures we were able to separate only some of the possible esters; however, the presence of fractions corresponding in boiling point, and the analyses of these fractions showed that all the esters specified by the ester mechanism are always formed in some quantity.

The fact of the formation of four esters and three ketones for all the binary mixtures of primary alcohols was a strong argument in favor of the assumption that the mixed ketone, as well as two symmetrical ketones, is obtained through the intermediate formation of esters.

The ester yields depended on the experimental conditions: they decreased with an increase of temperature, and increased with an increase of volume rate, i.e., with a decrease of the contact time.

Aldehydes, like the esters, were always observed among the reaction products. Curves expressing the relationship of the aldehyde yields to the experimental temperature usually had minima at temperatures identical or close to the temperatures corresponding to the maxima for the mixed ketone. The aldehyde yields increased with a decrease of contact time.

Apparently, a complex equilibrium exists in the ketonization reactions of mixtures of primary alcohols:

$$RCHO + R'CHO \underset{> t^\circ}{\rightleftarrows} RCOOCH_2R' \xrightarrow[> t^\circ]{} RCOR'.$$

With an increase of the temperature from 275 to 350°, a sharp decrease of the yields of the esters, and an increase of the yields of mixed ketones are observed. A further increase of the temperature led to a decrease of the yields of mixed ketones, and to an increase of the quantities of aldehydes, since with an increase of temperature the equilibrium is shifted toward the left, and dissociation of the esters with formation of aldehydes proceeds:

$$RCHO + R'CHO \underset{> t^\circ}{\rightleftarrows} RCOOCH_2R'.$$

An increase of the volume rate decreased the yields of mixed ketones and produced an increase of the quantities of aldehydes, since the contact time became inadequate for occurrence of the condensation reaction of aldehydes and of the ketonic decomposition of the esters.

Supplementarily introduced hydrogen had a favorable effect on the ketonization reaction; it reduced the quantity of aldehydes and sharply increased the yield of mixed ketone. On the contrary, in the operation without additional hydrogen a considerable increase of the aldehyde yields, and a decrease of the yields of mixed ketones was observed, i.e., the stage of further aldehyde transformations – condensation to esters and ketonic decomposition of the latter – was inhibited. Moreover, the reduction of the yields of gaseous products which occurred, indicated a gradual lowering of the activity of the catalyst.

Some rules regarding the effect of the composition of the initial mixture of alcohols were established. The optimum temperature for formation of the mixed ketone was shifted toward an increase, in proportion to the increase of the molecular weight and the increase of branching of the initial alcohols. Thus, for the formation of methyl propyl ketone from a mixture of ethyl and butyl alcohols the optimum temperature was 325°, for the formation of methyl isobutyl ketone from a mixture of ethyl and isoamyl alcohols it was 350°, and for the production of propyl isobutyl ketone from a mixture of butyl and isoamyl alcohols it was 375°. The maximum yields of mixed ketones were obtained at molar ratios, between the alcohol with a lower molecular weight and the alcohol with the higher molecular weight, equal to 2 : 1. Predominance of the alcohol with the higher molecular weight in the mixture led chiefly to the production of the symmetrical ketone corresponding to this alcohol. On the contrary, an increase of the content of the alcohol with the lower molecular weight in the initial mixture to a ratio of 3 : 1 or 5 : 1 usually led to some decrease of the yields of mixed ketone and to an increase of the yields of the symmetrical ketone corresponding to the alcohol with the lower molecular weight.

The presence of carbon dioxide in the resulting gaseous products, apparently indicated the use of the ester mechanism of the process, although the presence of 8-10% CO and the too-small quantities of olefins (3-4%), compels us to refer to it with caution, the more so since CO_2 can be produced by the water gas reaction from the CO and water which formed during the condensation:

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

where the quantities of CO_2 according to this reaction will be greater, the more thoroughly the condensation with formation of water proceeds, which was established by Bocharova and Dolgov [3]. In such a case the possibility of the occurrence of the process (possibly parallel) according to the Klyukvin-Ipatyev aldol scheme is not excluded, in favor of which is the small formation of olefins which, according to the ester scheme, should be obtained in an equimolar ratio to CO_2. The possibility of polymerization of the olefins was not excluded, especially since the high-boiling residue which we did not investigate amounted to 5-15% of the initial mixture.

Considering the complexity of the process of the transformation of primary alcohols to ketones, we nevertheless, possibly only temporarily, adhered to the ester mechanism of Sabatier-Kagan: alcohols → aldehydes → esters → ketones.

For example, the formation of methyl propyl ketone from a mixture of ethyl and n-butyl alcohols proceeds according to the scheme:

$$2C_2H_5OH \rightarrow 2CH_3CHO + 2H_2;$$
$$C_4H_9OH \rightarrow 2C_3H_7CHO + 2H_2;$$
$$2CH_3CHO \rightarrow CH_3COOC_2H_5;$$
$$2C_3H_7CHO \rightarrow C_3H_7COOC_4H_9;$$
$$CH_3COOC_2H_5 + C_3H_7COOC_4H_9 \rightarrow CH_3COC_3H_7 + CO_2 + C_2H_4 + C_4H_9OH.$$

The overall reaction is:

$$2C_2H_5OH + C_4H_9OH \rightarrow CH_3COC_3H_7 + CO_2 + C_2H_4 + 4H2.$$

The formation of a mixed ketone from a mixture of two primary alcohols may be represented in general form by the scheme:

$$2R'CH_2CH_2OH + R''CH_2CH_2OH \rightarrow R'CH_2COCH_2R'' + CO_2 + R'CH=CH_2 + 4H_2 (R' < R'').$$

Parallel reactions lead to the formation of symmetrical ketones, for example:

$$2CH_3COOC_2H_5 \rightarrow CH_3COCH_3 + CO_2 + C_2H_4 + C_2H_5OH,$$
$$2C_3H_7COOC_4H_9 \rightarrow C_3H_7COC_3H_7 + CO_2 + C_4H_8 + C_4H_9OH, \text{ etc.}$$

The majority of the intermediate and final products produced, which were specified by the present schemes, were separated and identified. Judging by the presence of the corresponding fractions and by the analysis of the fractions, the substances which we were unable to isolate because of analytical difficulties, were all apparently present in the reaction products.

Considering the extreme complexity of the process, and the possibility of the simultaneous occurrence of a large number of side reactions and secondary reactions, it was impossible to consider the scheme which we postulated as exhaustive. According to the experimental data obtained, they were only first approximations to a path to the complete discovery of the mechanism of the process.

EXPERIMENTAL

n-Butyl alcohol, which after drying over Na_2SO_4 and after distillation had a b. p. of 116.5-118.0°, d^{18} 0.806, and n_D^{18} 1.3997, and isoamyl alcohol, which after drying over Na_2SO_4 and after distillation had a b. p. of 130.5-132.0°, d^{18} 0.816 and n_D^{18} 1.4080, were used for carrying out the work. The experiments were carried out in the same apparatus which was used for ketonization of the previous mixtures [1, 2].

The liquid condensates from each experiment were fractionally distilled. The following fractions were obtained by the distillations: 1st 65-80°, 2nd 80-100°, 3rd 100-120°, 4th 120-132°, 5th 132-140°, 6th 140-146°, 7th 152-158°, 8th 160-170°, and 9th 170-199°; and the residue (above 199°). The fractions from all the experiments which were identical in boiling point, after analysis for ketones, aldehydes, and esters, were combined and fractionated once more for the purpose of separation of the individual substances and their identification.

1st Fraction. On redistillation a fraction corresponding to butyraldehyde was separated:

B. p. 73.5-74.5°, d_4^{20} 0.8176, n_D^{20} 1.3844.
Literature values: b. p. 74.7°, d_4^{20} 0.8170, n_D^{20} 1.38433.
2,4-Dinitrophenylhydrazone: m. p. 126.0-126.3° (according to literature data 126.0°).
Found %: N 22.40. $C_{10}H_{12}O_4N_4$. Calculated %: N 22.22.

The 2nd fraction was a mixture of butyraldehyde and isovaleraldehyde and water. On redistillation with other fractions, an isovaleraldehyde fraction was separated:

B. p. 91.5-92.5°, d_4^{20} 0.7899, n_D^{20} 1.3923.
Literature values: b. p. 92.5°, d_{20}^{20} 0.7845, n_D^{20} 1.39225.
2,4-Dinitrophenylhydrazone: m. p. 122.0-122.5° (according to literature data 123°).
Found %: N 21.19. $C_{11}H_{14}O_4N_4$. Calculated %: N 21.05.

The 3rd, 4th and 5th fractions contained the unreacted original alcohols, butyl (100-120°) and isoamyl (120-132° and 132-140°).

The 6th fraction contained dipropyl ketone, which was isolated and identified:

B. p. 143.5-144.5°, d_4^{20} 0.8175, n_D^{20} 1.4069.
Literature values: b. p. 144.1°, d_4^{20} 0.8175, n_D^{22} 1.40732.
Found: M 112.7, 113.7. $C_7H_{14}O$. Calculated: M 114. Semicarbazone after two recrystallizations had a m. p. of 133.5-134.0°, (according to literature data 133.0°).
Found %: N 24.51. $C_8H_{17}ON_3$. Calculated %: N 24.56.

The 7th fraction contained almost pure propyl isobutyl ketone, which was isolated by a second distillation, and had the constants:

B. p. 154-155°, d_4^{20} 0.8186, n_D^{20} 1.4106.
Literature data: b. p. 155° (750 mm), d_0^{22} 0.813.
Found: M 127.2, 129.8. $C_8H_{16}O$. Calculated: M 128.
The semicarbazone after three recrystallizations had a m. p. of 123.0-123.5° (according to literature data 123-124°).
Found %: N 22.91. $C_9H_{19}ON_3$. Calculated %: N 22.70.

The 8th fraction contained esters; according to the analytical data the butyl ester of butyric acid (b. p. 166.6°) was probably present. Moreover, this fraction contained a certain quantity of diisobutyl ketone (b. p. 168°), which was demonstrated by production of the 2,4-dinitrophenylhydrazone, which after recrystallization had a m. p. of 65-66° (66° according to the literature).

The 9th fraction consisted of esters. The closeness of the boiling point appeared to be the reason why, of the four esters the presence of which was extremely probable (butyl butyrate 166.6°, isoamyl butyrate 178.6°, butyl isovalerate 175.7°, and isoamyl isovalerate 190.4°), the first three were not isolated. On a second distillation we were able to obtain in only a small quantity a fraction which corresponded in constants to isoamyl isovalerate:

B. p. 188-190°, d_4^{20} 0.8572, n_D^{20} 1.4127.
Literature values: b. p. 190.4° $d_4^{18.7}$ 0.8583, $n_D^{18.7}$ 1.41300.

The residue (above 199°), according to analysis, contained esters and ketones; they were not studied further.

The composition of the gas from the experiments, the conditions of which were most favorable for production of the mixed ketone, was characterized by a considerable content of H_2 (80-83%) and CO (1-10%). It contained CO_2 in the quantity of 3-4%, olefins also 3-4%, but saturated hydrocarbons were absent.

SUMMARY

1. Molar ratios of n-butyl and isoamyl alcohols in the initial mixture, equal to 2 : 1 and 3 : 1, a temperature of 350-375°, and a volume rate of 100-150, were optimum conditions for the formation of propyl isobutyl ketone. The yields of propyl isobutyl ketone amounted to 15% of the initial mixture, dipropyl ketone about 22%, and diisobutyl ketone 2-3%. The total yield of ketones amounted to 40% of the initial mixture. At low temperatures (275-325°) esters were obtained in high yields (about 60%) of the initial mixture).

2. A general method of production of mixed ketones of the aliphatic series, including the passage of mixtures of primary alcohols over Dolgov and Bolotov's copper activated catalyst was proposed. The yields of the mixed ketones amounted to 20-25% of the initial mixture of alcohols (40-50% of the theoretical). The total yields of ketones, taking into account the formation of symmetrical ketones, amounted to 30-40% of the initial mixture (60-80% of the theoretical).

3. It was found that aldehydes and esters are intermediate products in the ketonization reaction of mixtures of primary alcohols over a copper activated catalyst.

4. Schemes of consecutive transformations of primary alcohols, known in the literature, were examined with consideration of the experimental data obtained. Results of the work essentially confirmed the validity of the Sabatier-Kagan ester mechanism. However, it is impossible to assume as completely excluded the possibility of a parallel occurrence of the process according to the Klyukvin-Ipatyev aldol scheme. Schemes of formation of mixed ketones from mixtures of primary alcohols were proposed.

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* T. p. = C. B. Translation pagination.

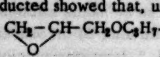
INVESTIGATIONS IN THE FIELD OF ASYMMETRICAL ORGANIC α-OXIDES

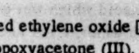
VIII. ISOMERIZATION OF THE ISOPROPYL ETHER OF GLYCIDOL AND ITS REACTION WITH AMMONIA

F. G. Ponomarev

In our previous works it was shown that the isopropyl ether of glycidol (I) adds amides of monobasic carboxylic acids [1] and diethylamine [2] with the formation of the corresponding nitrogenous derivatives of propanediol. The reaction of this ether of glycidol (I) with ethylenediamine was described somewhat earlier [3].

In the literature, other data relative to the transformations of this ether (I) are absent. In order to compare it with other asymmetrical α-oxides, it was of interest to study its behavior under the influence of different reagents.

The present report was devoted to an investigation of the transformations of the isopropyl ether of glycidol (I) under the action of aluminum oxide and zinc chloride, and also to the study of its reaction with ammonia. The experiments which we conducted showed that, under the influence of aluminum oxide and zinc chloride, the isopropyl ether of glycidol  $\underset{\diagdown O \diagup}{CH_2-CH}-CH_2OC_3H_7$-iso (I) isomerizes, according to the general scheme for monosubstituted ethylene oxide [4-6], chiefly to β-isopropoxypropionaldehyde (II) and, possibly, to a slight extent to isopropoxyacetone (III).



$\underset{\diagdown O \diagup}{CH_2-CH}-CH_2OC_3H_7$-iso; iso-$C_3H_7OCH_2-CH_2-CHO$; iso-$C_3H_7OCH_2-CO-CH_3$.

(I) (II) (III)

The structure of the resulting aldehyde (II) was demonstrated by its oxidation to β-isopropoxypropionic acid by a 1% solution of potassium permanganate. The β-isopropoxypropionic acid was identified as the silver salt.

With aqueous and alcoholic solutions of ammonia at room temperature the isopropyl ether of glycidol (I) forms the ether of aminopropanediol (IV), and possibly (V) and (VI):

$$NH_2CH_2-CHOH-CH_2OC_3H_7;\quad HN(CH_2-CHOH-CH_2OC_3H_7)_2;\quad N(CH_2-CHOH-CH_2OC_3H_7)_3.$$

(IV) (V) (VI)

The yield of the amino alcohol (IV) depends, as also from the reaction of ammonia with the methyl and ethyl ethers of glycidol, on the proportions of reagents [7]; but the isopropyl ether of glycidol reacts with ammonia somewhat more slowly since the reactivity of the ether oxides, as has already been recorded [8], decreases in a homologous series.

Formulas (IV-VI) for the resulting amino alcohols are assumed on the basis of the Krasusky law on the order of addition of ammonia to asymmetrical α-oxides [9].

The definite interest of this reaction resides in the fact that it discloses a possibility of synthesis by a relatively easy method of amino alcohols (IV) which are close to compounds of the $R-O-CH_2-CHOH-CH_2NR'R''$ type, which as is evident from the literature, possess an anesthetizing action [10].

The primary amine (IV) was separated in sufficiently pure form, but the secondary and tertiary amines (V and VI) were obtained as a mixture and were not separated.

The diacetate (VII) of iso-$C_3H_7-O-CH_2-CH(OCOCH_3)-CH_2-NHCOCH_3$, was obtained by the acetylation of amino alcohol (IV) by acetic anhydride.

The isopropyl ether of aminopropanediol (IV) possesses basic properties; it forms crystalline salts – the picrate and oxalate. It forms no crystalline derivatives with auric chloride, ethyl iodide, hydrogen chloride and phosphoric acid.

EXPERIMENTAL

Isomerization of the isopropyl ether of glycidol (I) under the influence of aluminum oxide and zinc chloride (in collaboration with Yu. I. Kazakov).

a) 30 g of the isopropyl ether of glycidol was passed (at the rate of 10 g) at 300° over aluminum oxide, precalcined at the indicated temperature. The isomerization experiments were carried out in a glass tube with an internal diameter of 13 mm; the catalyst was taken as 60% of the weight of the ether oxide. The tube was heated by an electric furnace equipped with a thermoregulator. The ether of glycidol was supplied dropwise from a funnel at a rate of 10 g per 40-45 minutes.

After passage of each 10 g of the substance (I) a renewal of the catalyst was made, since it was poisoned, being covered with a layer of resinous substances. From 30 g of the ether oxide, 26.7 g (89%) of condensate was obtained as a yellowish liquid, with a pungent odor, which was highly soluble in alcohol and in ether, but difficultly soluble in water. On distillation of the condensate 9 g of the isomerizate (30% of the ether oxide taken) as a colorless liquid with a b. p. of 78-80°, and 12 g (40%) of the unaltered ether oxide with an extended b. p. of 130-135° owing to admixture of aldehyde (II) and ketone (III) in it, were collected.

Investigation of the isomerizate (b. p. 78-80°). It gave a crimson coloration with fuchsin sulfurous acid, and a red coloration with sodium nitroprusside. It formed a silver mirror with an ammoniacal solution of silver oxide.

Oxidation. 98 ml of a 1% solution of potassium permanganate was added in small portions, with stirring, to 1 g of the substance, and the mixture was heated on a water bath for 30 minutes until the pungent odor characteristic of aldehydes had dissappeared. The filtrate was treated with an ammonia solution. After removal of the excess of the latter by heating the mixture on the water bath in a porcelain dish, 24 ml of a 10% solution of $AgNO_3$ (25% excess) was added to the neutral solution of the ammonium salt of β-isopropoxypropionic acid which was cooled to room temperature. The silver salt which precipitated at once was filtered off, washed with water, dried to constant weight in a desiccator over P_2O_5 in the dark, and analyzed.

0.3609 g sub.: 0.1656 g Ag. Found %: Ag 45.90. $C_6H_{11}O_3Ag$. Calculated %: Ag 45.14.

b) 4 g of the isopropyl ether of glycidol and 0.4 g of fused zinc chloride were placed in a flask equipped with a mechanical stirrer and a reflux condenser, and the mixture was heated for 4 hours at a bath temperature of 125°. About 1 g of the above-described isomerizate (with a b. p. of 78-81°), and 3.3 g (83%) of the ether oxide which was polymerized, were obtained.

Reaction of the isopropyl ether of glycidol with ammonia. Synthesis of 3-isopropoxypropanol-2-amine (IV) (in collaboration with I. K. Getmansky).

The experiments were carried out by the usual method [7]. Their results are recorded in the table.

Experiments	Used in the reaction (in g)			Reaction conditions		Yield of amino alcohol based on ether oxide taken (in %)
	ether of glycidol (I)	ammonia		ratio of ether oxide to ammonia (in parts by weight)	time (in hours)	
		aqueous 25%	alcoholic 9%			
1	10.0	1000	–	1:100	72	63
2	23.2	696	–	1:30	72	54
3	11.6	175	–	1:15	72	48
4	11.6	116	–	1:1	72	10
5	70.0	–	1400	1:20	48	48
6	35.0	–	350	1:10	48	37
7	35.0	–	175	1:5	48	22

In all these experiments, after distillation of the product (IV) a residue remained in the flask. The residue, judging by the analytical data for nitrogen, was a mixture of substances (V) and (VI).

3-Isopropoxypropanol-2-amine (IV) had the following constants:

B. p. 97-99° at 100 mm, d_4^{20} 0.9884, n_D^{20} 1.4535, MR_D 36.49; calc. 36.50.

0.2081 g sub.; 15.56 ml 0.1 N H_2SO_4. 0.2322 g sub.; 17.18 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1038 g sub.; 0.1806 g AgI. 0.1028 g sub.; 0.1796 g AgI (according to Zeisel). 0.1253 g sub.; 8.75 ml 0.1 N NaOH. 0.1145 g sub.; 8.02 ml 0.1 N NaOH [12]. 0.2034 g sub.; 28.15 g dioxane: Δt 0.30°. 0.1970 g sub.; 28.15 g dioxane: Δt 0.27°.

Found %: N 10.48, 10.37; C_3H_7O 43.93; OH 11.86, 11.90; M 128, 124. $C_6H_{15}O_2N$. Calculated %: N 10.52; C_3H_7O 44.46; OH 12.77; M 133.

3-Isopropoxypropanol-2-amine was a colorless liquid with a faint amine odor and a bitter, stinging taste. It had a great tendency toward supercooling, as a result of which it slowly (after a month) crystallized as colorless, acicular crystals which melted at 32°. We obtained this amino alcohol earlier, but it was characterized as a liquid [8]. It dissolved well in water, alcohol, and dioxane, but dissolved poorly in benzene; it did not dissolve in ether. It rapidly decolorized potassium permanganate and a chloroform solution of bromide. It gave characteristic reactions for the hydroxyl and primary amino groups (with metallic sodium, with sodium nitroprusside and acetone, with potassium hydroxide and chloroform) [11]. It was stable on long storage. Under ordinary conditions it absorbed CO_2 and H_2O from the air.

A weighed portion of 0.8660 g of the freshly-distilled substance, after 6, 24 and 36 hours, increased 16, 21 and 25% in weight, respectively.

The picrate of the amino alcohol, obtained by mixture of alcoholic solutions of equimolar quantities of product (IV) and picric acid, melted at 140-142° (from water).

0.0984 g sub.: 11.14 ml 0.1 N H_2SO_4. 0.1425 g sub.: 15.78 ml 0.1 N H_2SO_4 (according to Ekkert) [13]. Found %: N 15.86, 15.50. $C_{12}H_{18}O_9N_4$. Calculated %: N 15.45.

The oxalate of the base (IV) was obtained by heating solutions of the amino alcohol and oxalic acid (m. p. 189°) in anhydrous ether on the water bath for 2 hours, or in anhydrous toluene at 90° for 15 minutes. After two recrystallizations from anhydrous alcohol it melted at 148-149°.

0.1612 g sub.: 7.25 ml 0.1 N H_2SO_4. 0.1599 g sub.: 7.08 ml 0.1 N H_2SO_4 (according to Kjeldahl). Found %: N 6.29, 6.20. $C_8H_{17}O_6N$. Calculated %: N 6.27.

Acetylation of the amino alcohol (IV). The diacetate was obtained as a colorless, syrupy liquid by the action of freshly-distilled acetic anhydride (20% excess) on the amino alcohol:

B. p. 158-161° at 6 mm, d_4^{20} 1.0456, n_D^{20} 1.4491, MR_D 55.75; calc. 55.29.
0.1415 g sub.: 6.1 ml 0.1 N H_2SO_4. 0.2072 g sub.: 9.09 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1426 g sub.: 1.297 ml 1 N KOH. Found %: N 6.04, 6.23; CH_3CO 39.13. $C_{10}H_{19}O_4N$. Calculated %: N 6.44; CH_3CO 39.63.

The diacetate dissolved well in ether, dioxane and benzene, contained no free hydroxyl groups, and gave no characteristic reactions for the primary amino group [11].

SUMMARY

1. The isomerization of the isopropyl ether of glycidol under the action of aluminum oxide and zinc chloride was studied.

It was shown that under the influence of these catalysts the ether oxide was isomerized chiefly to β-isopropoxypropionaldehyde, and possibly to a small extent to isopropoxyacetone.

2. The reaction of the isopropyl ether of glycidol with aqueous and alcoholic solutions of ammonia was studied.

The chief product of this reaction, 3-isopropoxypropanol-2-amine, was isolated and characterized. Its diacetate and some of its salts were described.

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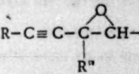
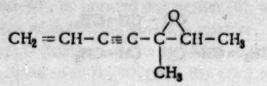
ISOMERIZATION OF α-OXIDES OF THE ACETYLENE AND VINYLACETYLENE SERIES

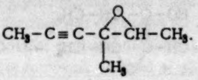
F. Ya. Perveev and N. I. Kudryashova

It was found earlier [1-5] that, by isomerization under the action of zinc chloride, α-oxides of the  type form an acetylenic aldehyde or ketone, depending on the structure of the initial oxide.

It was the purpose of the present work to study the isomeric transformations of oxides of the acetylene and vinylacetylene series, under the action of dilute sulfuric acid. 3-Methyl-epoxy-2,3-hepten- 6-yne-4 (I) [6] and 3-methyl-epoxy-2,3-hexyne-4 (II) [7] were used for the investigation:



(I)



(II)

A ketone, which was mobile and had the pungent odor of a liquid possessing lachrymatory properties, was formed by isomerization of 3-methyl-epoxy-2,3-hepten-6-yne-4 in acetic anhydride in the presence of a few drops of sulfuric acid. With semicarbazide it readily formed the semicarbazone. Even on long contact with an alcoholic solution of ferric chloride it gave no coloration. Its structure was demonstrated by oxidation. Methyl ethyl ketone and oxalic acid were among the oxidation products.

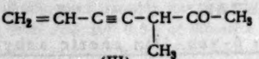
On the basis of the data obtained, we attributed the structure corresponding to the unsaturated ketone, 3-methyl-hepten-6-yne-4-one-2 (III), to the compound synthesized.

The methyl ethyl ketone formed as a result of the decarboxylation of the β-keto acid.

On isomerization of the same oxide by an aqueous solution of sulfuric acid, after repeated distillation two fractions were separated: 1st, b. p. 40° (3 mm); 2nd, b. p. 53-54° (1 mm).

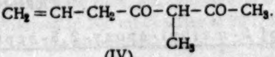
According to its physical constants, the 1st fraction corresponded to 3-methyl-hepten-6-yne-4-one-2 (III). A test of a mixture of the semicarbazone with the semicarbazone obtained from substance (III) produced no melting point depression.

The 2nd fraction was a mobile liquid, which became yellow on standing, and gradually polymerized. It gave an intense violet coloration with an alcoholic solution of ferric chloride. Its elementary composition corresponded to the formula $C_8H_{12}O_2$. It could be assumed that we were dealing with the β-diketone (IV), which could be obtained by hydration of the triple bond in the presence of sulfuric acid:



$CH_2=CH-C\equiv C-\underset{CH_3}{\underset{|}{CH}}-CO-CH_3$

(III)

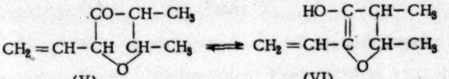


$CH_2=CH-CH_2-CO-\underset{CH_3}{\underset{|}{CH}}-CO-CH_3.$

(IV)

The substance was hydrogenated in methyl alcohol over Raney nickel in order to demonstrate its structure. Hydrogen was consumed in the quantity calculated for two double bonds. No further addition of hydrogen occurred. The hydrogenation product gave no coloration of enol with $FeCl_3$. It did not react with hydroxylamine and semicarbazide. The active hydrogen content, determined by the Terentyev-Shcherbakova method, corresponded to one hydroxyl group. The substance was not dehydrated (recovered unchanged) by heating with a 30% solution of sulfuric acid.

All the data cited indicated that the substance which we separated from the 2nd fraction was not the β-diketone. In addition, the isomerization product obtained with hydroxylamine gave an oxime, whereas the product of the reaction of the β-diketone with hydroxylamine is probably isooxazole. All this enabled us to assume that, together with the formation of the unsaturated ketone (III), tetrahydro-β-ketofuran (V), chiefly, with an admixture of its enolic form (VI), was obtained on isomerization of the α-oxides with 30% sulfuric acid:

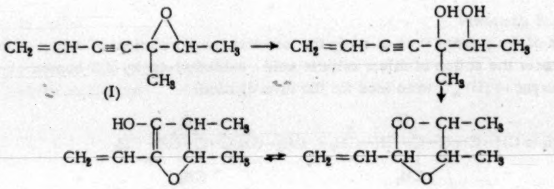


(V) (VI)

The per cent of the enolic form in the tautomeric mixture, determined by the Terentyev-Shcherbakova method, was equal to 53.8.

By the ozonization method it was demonstrated that there is a double bond in the side chain (quantity of formaldehyde determined was 47%). The capacity of the tetrahydro-β-ketofurans for enolization was first established by Dupont [8].

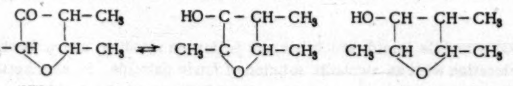
Apparently, the formation of the vinylalkyltetrahydro-β-ketofurans proceeds as follows:



(I) (VI) (V)

The easy mobility of the hydroxyl situated in the α-position to the triple bond was recorded in Nazarov's works [9] on the syntheses and transformations of divinyl ketones. A similar transformation confirmed the fact that, on treatment of a glycol with an aqueous solution of 30% sulfuric acid, the same compounds were formed, but with a higher content of tetrahydro-β-ketofuran.

On treatment of 3-methyl-epoxy-2,3-hexyne-4 (II) with an aqueous solution of 20% sulfuric acid, and as a result of repeated distillation of the reaction products, a substance which was a liquid with a specific odor, and which gave a violet coloration with ferric chloride, was obtained. The enol content, determined by the Terentyev-Shcherbakova method, amounted to 85-89%. The elementary composition corresponded to the formula $C_7H_{12}O_2$. On hydrogenation over Raney nickel, hydrogen was absorbed in the quantity required for one double bond. The hydrogenation product was not dehydrated by 30% sulfuric acid. It did not react with hydroxylamine and semicarbazide. With phenyl isocyanate it formed phenylurethan which melted at 86-87° (from ligroin). On the basis of the data obtained, we attributed the structure of tetrahydro-β-ketofuran (VII) to the substance synthesized, and the structure of tetrahydro-β-hydroxyfuran (VIII) to its hydrogenation product:



(VII) (VIII)

EXPERIMENTAL

Isomerization of 3-methyl-epoxy-2,3-hepten-6-yne-4 in acetic anhydride.

20 g of acetic anhydride with 3 drops of H_2SO_4 was placed in a round-bottomed flask with a mechanical stirrer and, with constant stirring, 15 g of the oxide was added gradually. An appreciable evolution of heat resulted. After addition of all the oxide, the reaction mixture was heated on the water bath for 10 minutes, then the reaction product was washed several times with water, and was vacuum steam-distilled. The distilled substance was extracted with ether and dried with Na_2SO_4; the ether was removed, and the substance which remained was vacuum distilled.

A substance with a b. p. of 57-58° at 9 mm was separated after repeated distillation.

n_D^{16} 1.4860; d_4^{16} 0.9091; MR_D 38.5. $C_8H_{10}O$ ⊧ ⊧ Calc. 36.7.

0.1003 g sub.: 0.2894 g CO_2; 0.0751 g H_2O. 0.1038 g sub.: 0.2980 g CO_2; 0.0793 g H_2O. Found %: C 78.47, 78.35; H 8.40, 8.55. $C_8H_{10}O$. Calculated %: C 78.63; H 8.25.

The semicarbazone was recrystallized twice from aqueous alcohol. Its m. p. was 156° (decomp).

0.0924 g sub.: 19.5 ml N_2 (21.5°, 741.2 mm). 0.0937 g sub.: 19.5 ml N_2 (21°, 749.8 mm). Found %: N 23.51, 23.47. $C_9H_{13}ON_3$. Calculated %: N 23.41.

The oxidation of 3-methyl-hepten-6-yne-4-one-2 was carried out in the cold with potassium permanganate. For the oxidation, 5 g of the ketone was used, and 35.8 g of $KMnO_4$ (34.5 g was required) was used. The manganese dioxide was filtered off, and washed with hot water. No neutral products were observed in the filtrate. The solution was evaporated to a small volume, acidified with 10% H_2SO_4 and boiled under reflux for 2 hours. The cooled solution was alkalized and the neutral products were again driven off in a solution of 2,4-dinitrophenylhydrazine. The precipitate which came down was recrystallized from alcohol, and its m. p. was 110-111°; a test of a mixture with the known, prepared 2,4-dinitrophenylhydrazone of methyl ethyl ketone gave no melting point depression.

None of the volatile acids was detected. The portion of the acidified solution which remained was extracted with ether in an extractor. Oxalic acid, which melted at 182° after 3 sublimations, was separated.

Cyclization of 3-methyl-epoxy-2,3-heptene-6-yne-4

150 ml of water acidified with 2-3 drops of H_2SO_4 was placed in a round-bottomed flask with a mechanical stirrer, and 60 g of the oxide was added gradually. From time to time the mixture was cooled with water, lest the temperature exceed 30-40°, as pointed out earlier [6]; a glycol formed under these conditions. Then 12 ml more of concentrated H_2SO_4 was added to the reaction mixture. Stirring was continued for about 3 hours. The upper layer was separated and steam-distilled until a negative reaction for enol was obtained. The resulting substance was extracted with ether, dried over Na_2SO_4, and the ether was removed. A total of 45 g of a product was separated, which was distilled.

The 1st fraction had a b. p. of 40° (3 mm); the 2nd fraction had a b. p. of 53-54° (1 mm).

The 1st fraction (n_D^{20} 1.4832 d_4^{20} 0.9068,) corresponded to the unsaturated ketone, 3-methyl-hepten-6-yne-4-one-2.

Analysis of the 2nd Fraction

n_D^{20} 1.4985; d_4^{20} 0.9903; MR_D 41.53. $C_8H_{12}O_2F_2$. Calc. 39.18.

0.1063 g sub.: 0.2670 g CO_2; 0.0836 g H_2O. 0.1065 g sub.: 0.2668 g CO_2; 0.0854 g H_2O. 0.1310 g sub.: 11.7 ml CH_4 (16.5°, 760.3 mm). 0.1238 g sub.: 11.3 ml CH_4 (16°, 748.6 mm). 0.1228, 0.1864 g sub.: 14.36 g benzene: Δt 0.31, 0.47°. Found %: C 68.54, 68.37; H 8.80, 8.97; active H 0.376, 0.376. M 141.5, 141.7. $C_8H_{12}O_2$. Calculated %: C 68.51; H 8.63. M 140.2.

The oxime, recrystallized from alcohol, melted at 129-130°.

0.1014 g sub.: 7.9 ml N_2 (20.5°, 762.5 mm). 0.1832 g sub.: 14.1 ml N_2 (18°, 761.2 mm). Found %: N 8.96, 8.94. $C_8H_{13}O_2N$. Calculated %: N 9.02.

Ozonization. In order to demonstrate the position of the double bond, the resulting product was ozonized in chloroform. 5 g of the substance, dissolved in 41 g of chloroform, was used for the ozonization. 2.12 g of ozone was passed for the ozonization, whereas 1.71 g was required for one double bond. The ozonide was decomposed with water. From the ozonolysis products formaldehyde was determined by condensation with dimedon.

For this, the decomposed ozonide was poured into a volumetric flask, and diluted with water to 150 ml. 10 ml was taken from the total quantity; 0.5 g of dimedon was dissolved in 100 ml of water at 90°. 10 ml of the solution of ozonolysis products was added to the dimedon solution, and the solution was heated for 1 hour at 60-70°. The precipitate which came down was filtered off, washed with hot water, and dried at 60-70°. After recrystallization from methyl alcohol the condensation product melted at 188-188.5°. A test of a mixture with the known, prepared compound gave no melting point depression. 0.1067 g of the dimedon condensation product in 10 ml corresponded to 0.1629 g of formaldehyde in 150 ml of ozonolysis products. Formic acid was determined by the Fink method. 0.7168 g of calomel from 20 ml of the ozonolysis product corresponded to 0.5242 g of formic acid, or 0.3418 g of formaldehyde in 150 ml of the ozonide.

In all, 0.5047 g (47.1%) of formaldehyde was determined in the ozonized products.

Hydrogenation of the cyclization product. 13.75 g of the substances was used for the hydrogenation, which was carried out in methyl alcohol over Raney nickel. 4813 ml of hydrogen was consumed, whereas 4783 ml of hydrogen was required theoretically for 2 double bonds. A colorless product with a b. p. of 66-67° at 2 mm was separated:

n_D^{20} 1.4595; d_4^{20} 0.9695; MR_D 40.55. $C_8H_{16}O_2$. Calc. 40.11.

With $FeCl_3$ the hydrogenation product gave no coloration for enol, and it did not react with hydroxylamine and semicarbazide.

0.1398, 0.1493 g sub.: 20.2, 21.2 ml CH_4 (14°, 770.5 mm). Found %: active H 0.619, 0.608. $C_8H_{16}O_2$. Calculated %: active H 0.699.

The original alcohol was recovered by heating the hydrogenation product with 30% sulfuric acid:

B. p. 69-71° at 2 mm; n_D^{20} 1.4565.

0.1536 g sub.: 22.5 ml CH_4 (16°, 765.6 mm). 0.1577 g sub.: 22.9 ml CH_4 (17°, 765.6 mm). Found %: active H 0.618, 0.608. $O_8H_{16}O_2$. Calculated %: active H 0.699.

Cyclization of 3-methyl-epoxy-2,3-hexyne-4

150 ml of 20% sulfuric acid was placed in a round-bottomed flask, and 20 g of the oxide was added gradually. A strong evolution of heat was observed. After addition of the oxide, the reaction mixture was boiled under reflux for 40-45 minutes. After this the reaction product was steam-distilled at constant volume. The resulting substance was extracted with ether and dried; the ether was removed and the product was vacuum distilled. 16 g of a substance was separated:

B. p. 48-49° at 4 mm; n_D^{20} 1.4560; d_4^{20} 0.9592; MR_D 36.40. $C_7H_{12}O_2F$. Calc. 35.33.

0.1016 g sub.: 16.1 ml CH_4 (11°, 749.8 mm). 0.1074 g sub.: 17.9 ml CH_4 (11.5°, 749.8 mm). Found %: active H 0.669, 0.702, which amounted to 85.1, 89.2 of enol, respectively. $C_7H_{12}O_2$. Calculated %: active H 0.784.

Hydrogenation was carried out in methyl alcohol over Raney nickel. 12.67 g of the substance was used, and 2350 ml of hydrogen was passed for hydrogenation; 2358 ml of hydrogen (15°, 753 mm) was required for the hydrogenation. The hydrogenation product was vacuum distilled:

B. p. 86-87° at 13 mm; n_D^{20} 1.4380; d_4^{20} 0.9476; MR_D 36.16. $C_7H_{14}O_2$. Calc. 36.18.

0.1073 g sub.: 19.5 ml CH_4 (11°, 769.9 mm). 0.0704 g sub.: 13.0 ml CH_4 (11.5°, 769.9 mm). Found: active H 0.786, 0.799. $C_7H_{14}O_2$. Calculated %: active H 0.774. 0.1021 g sub.: 0.2422 g CO_2; 0.0980 g H_2O. 0.1051 g sub.: 0.2482 g CO_2; 0.0994 g H_2O. Found %: C 64.73, 64.45; H 10.74, 10.59. $C_7H_{14}O_2$. Calculated %: C 64.57; H 10.84.

Phenylurethan. A mixture of 1 g of phenol isocyanate and 1 g of the substance was left for 12 days in a sealed ampoule. Then the ampoule was heated for 10 minutes on the water bath. After the contents of the ampoule head crystallized, the precipitate was filtered off and recrystallized from ligroin. The m. p. was 86-87°.

0.1553 g sub.: 8.0 ml N_2 (17°, 738.2 mm). Found %: N 5.82. $C_{14}H_{19}O_3N$. Calculated %: N 5.62.

SUMMARY

1. The tri-substituted oxides of the acetylene and vinylacetylene series were transformed to the corresponding tetrahydro-β-ketofurans by reaction with dilute sulfuric acid, the reaction of formation of which proceeded via the glycol.

2. 2-Vinyl-4,5-dimethyl-tetrahydro-3-ketofuran and 2,4,5-trimethyltetrahydro-3-ketofuran, which were not described in the literature, and also their hydrogen products, 2-ethyl-4,5-dimethyl-tetrahydro-3-hydroxyfuran and 2,4,5-trimethyltetrahydro-3-hydroxyfuran, were isolated.

3. The non-enolizing ketone, 3-methyl-hepten-6-yne-4-one-2, was formed by the isomerization of 3-methyl-epoxy-2,3-hepten-6-yne-4 in acetic anhydride in the presence of sulfuric acid.

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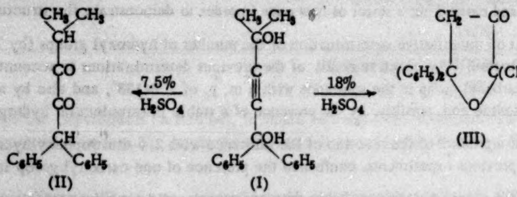
TRANSFORMATION OF ASYMMETRICAL DIMETHYLDIPHENYLBUTYNEDIOL IN AN ACID MEDIUM

IV. 2-METHYL-5,5-DIPHENYLPENTEN-4-OL-2-ONE-3

E. D. Venus-Danilova, V. I. Ryabtseva and L. A. Grigoryeva

The isomerization of asymmetrical dimethyldiphenylbutynediol (2-methyl-5,5-diphenylpentyne-3-diol-2,5) (I) to the saturated α-diketone with an open chain of carbon atoms – 2-methyl-5,5-diphenylpentanedione-3,4 (m. p. 132-133°) (II) – and to a ketone of the tetrahydrofuran series – 2,2-dimethyl-5,5-diphenyltetrahydrofuranone-3 (m. p. 66-67°) (III) – was described earlier [1].

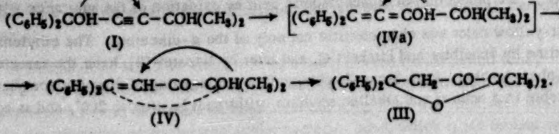
It was observed that a 7.5% alcoholic solution of sulfuric acid converted the glycol only to the diketone, but that an 18% solution converted it to the substituted tetrahydrofuranone. At intermediate sulfuric acid concentrations a mixture of two substances, with a m. p. of 132-133° and a m. p. of 66-67°, was obtained, in which the yield of the cyclic ketone increased, and that of the diketone decreased, with an increase of the acid concentration.



A further investigation of these transformations, carried out after publication [1], showed that the substance with a m. p. of 132-133° (II) was converted completely to the substance with a m. p. of 66-67° (III) on heating with a 20% alcoholic solution of sulfuric acid.

This fact placed in doubt the problem of the structure of Substance (II), since the diketone should form as a result of a simultaneous bilateral acetylene-allene rearrangement of the glycol, and consequently, is the end product of its isomerization and cannot be converted to tetrahydrofuranone. The tetrahydrofuranones, as shown by Nazarov's works [2], are obtained as a result of the cyclization of unsaturated α-keto alcohols, which are the primary products of the isomerization of the asymmetrical acetylenic γ-glycols, i.e., the products of their acetylene-allene rearrangement. Moreover, in comparison with that required for a unilateral rearrangement which proceeds under milder conditions, an increased sulfuric acid concentration is required for carrying out a bilateral acetylene-allene rearrangement. According to data of the same Report I [1], the diketone (II) developed in 7.5% sulfuric acid, but the tetrahydrofuranone (III) was the product of the cyclization of the unsaturated keto alcohol in the 18% acid.

Proceeding from these considerations, it seemed to us more plausible to assign the structure of the ethylenic α-keto alcohol (IV) to the substance with the m. p. of 132-133°, which formerly was mistaken for the diketone (II). It is possible to assume the following scheme for the isomerization of the acetylenic γ-glycols to the unsaturated γ-keto alcohol (IV) and further to the substituted tetrahydrofuranone (III):



$$\underset{(I)}{(C_6H_5)_2COH-C\equiv C-COH(CH_3)_2} \longrightarrow \Big[\underset{(IVa)}{(C_6H_5)_2C=C=COH-COH(CH_3)_2}\Big] \longrightarrow$$

$$\longrightarrow \underset{(IV)}{(C_6H_5)_2C=CH-CO-COH(CH_3)_2} \longrightarrow \underset{(III)}{(C_6H_5)_2C-CH_2-CO-C(CH_3)_2}$$

As a result of a unilateral acetylene-allene rearrangement, the unstable hydroxyallene (IVa) develops first, which being the enolic form of the unsaturated α-keto alcohol, was converted to the keto alcohol (IV). At a low sulfuric acid concentration (7.5%) this keto alcohol is the sole product of the isomerization of the acetylenic

γ-glycol. With an increase of the acid concentration the cyclization of the keto alcohol [2] proceeds with the formation of tetrahydrofuranone (III).

The simultaneous bilateral acetylene-allene rearrangement of asymmetrically constructed γ-glycols of the acetylene series, with the intermediate formation of dienols, and further, diketones, seemed to us less likely under our conditions. The presence of the considerable dipole moment, and consequently, of the unequal valency of the two hydroxyl groups of these glycols should be considered. Such a bilateral rearrangement is possible for symmetrical γ-glycols of the acetylene series, and leads to diketones, as was observed but incorrectly interpreted by Krestinsky and Bazhenova-Kozlovskaya [3], by the action of formic acid on tetramethylbutynediol.

In Report I [1] the diketone structure was attributed to the substance with a m. p. of 132-133° on the basis of the following data:

1) a negative qualitative reaction with the Grignard reagent for the hydroxyl group;

2) obtaining of the dioxime;

3) obtaining of benzophenone, acetone and oxalic acid by oxidation with potassium permanganate;

4) obtaining of diphenylacetic acid by oxidation with chromic anhydride;

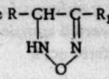
5) the green-yellow color of the substance.

However, on their critical consideration, none of these arguments are sufficiently conclusive; therefore, we were occupied with a detailed investigation of the substance with a m. p. of 132-133°, and repeated some of the previous experiments and carried out a series of new ones in order to demonstrate the structure of this product.

It was found that on quantitative determination of the number of hydroxyl groups (by Terentyev's method), one hydroxyl group was detected. The negative result of the previous determinations is accounted for, in all probability, by the presence of a carbonyl group in the substance with a m. p. of 132-133°, and also by an insufficient quantity of methylmagnesium iodide and, possibly, by the presence of a stable intramolecular hydrogen bond.

The obtaining of a product of the reaction of the substance with 2,4-dinitrophenylhydrazine, and also of the semicarbazone in the previous experiments, confirmed the presence of one carbonyl group in the substance.

With respect to the dioxime, it was probable that its formation did not take place, but that, instead of it, the isomeric dioxime was substituted 2,3-dihydro-1,2,5-oxdiazole



$R-CH-C-R_1$ (ring: $HN-O-N$) was formed. This substance could form as a consequence of the reaction of the unsaturated α-keto alcohol with two molecules of hydroxylamine at the carbonyl and at the double bond, with further cyclization, since the reaction was carried out under very severe conditions.

The original substance was not obtained on heating the reaction product of the substance (m. p. 132-133°) and hydroxylamine with dilute sulfuric acid in order to hydrolyze the dioxime, but strong resinification resulted.

Benzophenone, acetone and oxalic acid could be obtained not only by oxidation of the dienol form of the diketone, but also by oxidation of the ethylenic α-keto alcohol (IV) by potassium permanganate.

With respect to the formation of diphenylacetic acid, obtained by the oxidation of the substance with a m. p. of 132-133° by chromic anhydride, in order to account for its formation it is possible to assume a preliminary hydration of the α-keto alcohol, not according to the Markownikoff rule, as a consequence of its unique structure, and a further oxidation of the dehydration product with the formation of diphenylacetic and hydroxyisobutyric acids; acetone formed from the latter under the conditions of the reaction. Additional experiments were required in order to account for the production of diphenylacetic acid by oxidation of the substance with a m. p. of 132-133°.

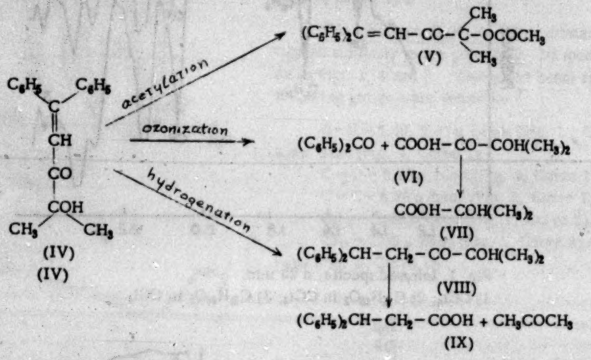
A light-yellow color was characteristic not only of the α-diketones. The ethylenic α-keto alcohols, synthesized for the first time by Scheibler and Fischer [4], and later by Nazarov [2], have the same color. It should be noted that 2-methyl-5-phenylpentene-4-ol-2-one-3, obtained by condensation of dimethylacetylenecarbinol with benzaldehyde, is entirely stable in a neutral and alkaline medium, withstands heating to 200°, and is completely cyclized in an acid medium [2].

In addition to carrying out the previous experiments for the substance with a m. p. of 132-133°, we obtained the acetate of this substance, and carried out an ozonolysis and a catalytic hydrogenation.

The acetate (m. p. 72-73°) (V) was synthesized by the action of acetic anhydride on the substance with a m. p. of 132-133°. The composition of the ester was confirmed by analysis. On hydrolysis of the ester, the original substance with a m. p. of 132-133° was formed.

Benzophenone and α-hydroxyisobutyric acid (VII), which formed as a result of the decomposition of β-methyl-β-hydroxy-α-ketobutyric acid (VI), were obtained by ozonization of the substance with a m. p. of 132-133°.

In the presence of colloidal palladium, the product with a m. p. of 132-133° was hydrogenated to the saturated α-keto alcohol (m. p. 66-67°) (2-methyl-5,5-diphenylpentanol-2-one-3 (VIII), the structure of which was demonstrated by oxidation by lead tetraacetate, to β,β-diphenylpropionic acid (IX) and acetone.


$(C_6H_5)_2C=CH-CO-C(CH_3)_2-OCOCH_3$
(V)
C_6H_5 C_6H_5
C
CH
CO
COH
CH_3 CH_3
(IV)
(IV)
acetylation
ozonization
hydrogenation
$(C_6H_5)_2CO + COOH-CO-COH(CH_3)_2$
(VI)
$COOH-COH(CH_3)_2$
(VII)
$(C_6H_5)_2CH-CH_2-CO-COH(CH_3)_2$
(VIII)
$(C_6H_5)_2CH-CH_2-COOH + CH_3COCH_3$
(IX)

On the basis of all the experiments carried out, it should be considered as demonstrated that the substance with a m. p. of 132-133° is not the diketone (II), but is the ethylenic α-keto alcohol, 2-methyl-5,5-diphenylpenten-4 ol-2-one-3 (IV).

If the saturated α-diketone (II) structure belonged to the original substance (m. p. 132-133°), neither an ester nor α-hydroxyisobutyric acid on ozonization of the substance with a m. p. of 132-133°, nor the β,β-diphenylpropionic acid by oxidation of the reduction product of the substance with a m. p. of 132-133° by lead tetraacetate, could be obtained.

Investigation of the Infrared and Ultraviolet Spectra

For confirmation of the structure of the substance $C_{18}H_{18}O_2$ (m. p. 132-133°) as the unsaturated α-keto alcohol, 2-methyl-5,5-diphenylpenten-4-ol-2-one-3 (IV), its infrared spectrum* was studied. The spectrum of a specially synthesized [2] α-keto alcohol, $C_{12}H_{14}O_2$ [$(CH_3)_2COH-CO-CH=CH-C_6H_5$], 2-methyl-5-phenylpenten-4-ol-2-one-3 (m. p. 39-40°), was obtained for comparison.

The spectra were taken with an "Infrared Monochromator" ISP-14^b apparatus with a quartz prism for wavelengths up to 3.5μ and with a rock salt prism for waves from 5μ and above.

The substance $C_{18}H_{18}O_2$. The absorption spectrum was obtained in the region from 1 to 2.5μ and from 5 to 9μ.

The spectrum of the substance in carbon tetrachloride (saturated solution) is given in Fig. 1 (Curve 2); the prism was of quartz, and the cuvette had a depth of 20 mm. As is evident from Fig. 1 (Curve 2), the substance had absorption bands at 1.49, 1.68, 1.76 and 2.07μ. The 1.49μ band is characteristic of the O−H group (first overtone ν); the 2.07 τ band (ν + δ) is also characteristic of this group. The 1.68μ band corresponds to the benzene ring, and the 1.76μ band corresponds to the methyl group. For comparison, the spectrum of the solvent, carbon tetrachloride, was presented (Fig. 1, Curve 1).

The presence of the hydroxyl group was also confirmed by the 2.9μ band (fundamental tone). This band is represented in Fig. 2 (Curve 1). In this case the substance, dissolved in carbon tetrachloride, was photographed by points; the cuvette had a depth of 1.0 mm. It should be noted that the 2.9μ band was relatively wide. This enabled us to assume the presence in the substance of an intramolecular hydrogen bond, which is not broken on dissolving in

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* The spectra were investigated by V. N. Nikitiny, to whom we express our deep appreciation.

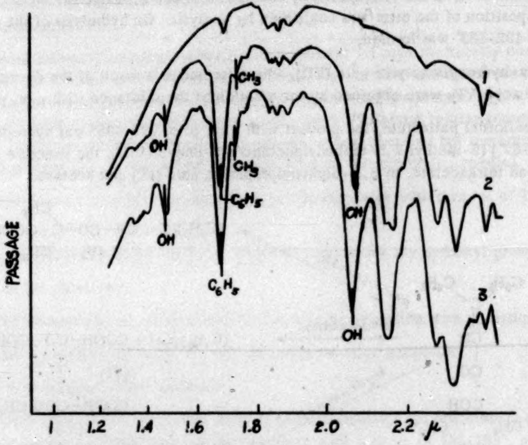

Fig. 1. Infrared spectra; d 20 mm.
1) CCl_4, 2) $C_{18}H_{18}O_2$ in CCl_4, 3) $C_{12}H_{14}O_2$ in CCl_4.

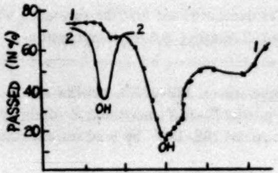

Fig. 2. Infrared spectra; d 1.0 mm.
1) $C_{18}H_{18}O_2$ in CCl_4, 2) C_2H_5OH in CCl_4.

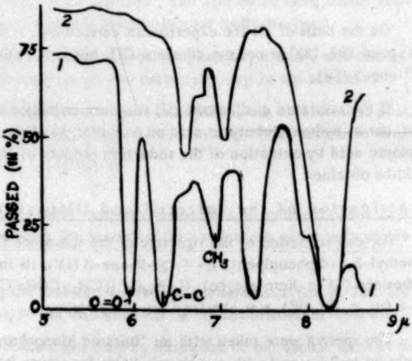

Fig. 3. Infrared spectra; d 0.158 mm.
1) $C_{18}H_{18}O_2$ in $CHCl_3$, 2) $CHCl_3$.

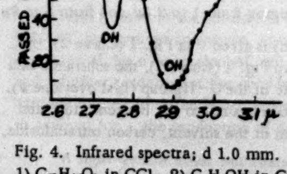

Fig. 4. Infrared spectra; d 1.0 mm.
1) $C_{12}H_{14}O_2$ in CCl_4, 2) C_2H_5OH in CCl_4.

carbon tetrachloride. For comparison, the hydroxyl group band of the ethylenic alcohol, dissolved in carbon tetrachloride, is given in Fig. 2 (Curve 2). This band is considerably narrower, since in this case there are no hydrogen bonds, and it is located at 2.75 μ.

The absorption spectrum of the substance dissolved in chloroform is presented in Fig. 3 (Curve 1). The spectrum was photographed by points with the rock salt prism, and a cuvette depth of 0.158 mm. The 5.98 μ absorption band characterized the vibration of the C=O bond, and the 6.34 and 6.95 μ bands belonged to the C=C and the CH_3 groups, respectively. In order to be sure that the bands observed did not pertain to chloroform, the spectrum of pure chloroform in a layer of 0.158 mm was taken (Fig. 3, Curve 2).

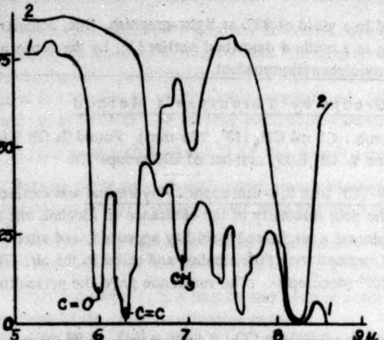

Fig. 5. Infrared spectra; d 0.158 mm.
1) $C_{12}H_{14}O_2$ in $CHCl_3$, 2) $CHCl_3$.

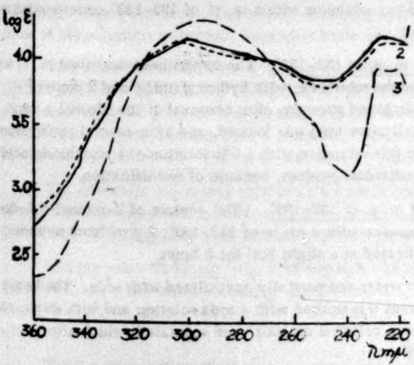

Fig. 6. Ultraviolet spectra in alcohol.
1) 2-Methyl-5,5-diphenylpenten - 4-ol-2; 2) acetate of 2-methyl- -5,5-diphenylpenten - 4-ol-2-one-3; 3) 2-methyl-5-phenylpenten- -4-ol-2-one-3.

Thus, the absorption spectra of the substance $C_{18}H_{18}O_2$ indicated the existence of the following groups:

O–H – 1.49, 2.07 μ bands (Fig. 1, Curve 2) and 2.9 μ (Fig. 2, Curve 1),

C=O – 5.98 μ band (Fig. 3, Curve 1),

C=C – 6.34 μ band (Fig. 3, Curve 1), C_6H_5 – 1.68 μ band (Fig. 1, Curve 2),

CH_3 – 1.76 μ band (Fig. 1, Curve 2) and 6.95 μ (Fig. 3, Curve 1).

The substance $C_{12}H_{14}O_2$. This substance was investigated similarly to the preceding. Its spectra are recorded in Figs. 1, 4 and 5. Absorption bands related to the following groups were determined:

O–H – 1.49, 2.07 μ bands (Fig. 1 , Curve 3) and 2.9 μ band (Fig. 4, Curve 1),

C=O – 5.98 μ band (Fig. 5, Curve 1),

C=C– 6.28 μ band (Fig. 5, Curve 1),

C_6H_5 – 1.68 μ band (Fig. 1, Curve 3),

CH_3 – 1.76 μ band (Fig. 1, Curve 3) and 6.92 μ band (Fig. 5, Curve 1).

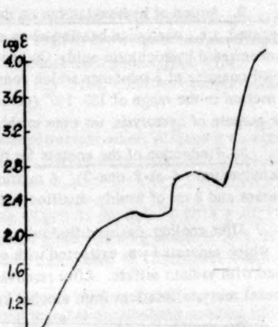

Fig. 7. Ultraviolet spectrum of 2-methyl-5,5- -diphenylpentanol-2-one-3 in alcohol.

The absorption spectra of the substances $C_{18}H_{18}O_2$ and $C_{12}H_{14}O_2$, which of course have the same functional groups, were close, since they differ by only one phenyl radical.

The ultraviolet spectra were photographed with an SF-4* spectrophotometer.

The absorption curves of alcoholic solutions of 2-methyl-5,5-diphenylpenten - 4-ol-2-one-3 (Substance IV) (Curve 1), its acetate (Substance V) (Curve 2), and 2-methyl-5-phenylpenten - 4-ol-2-one-3 (Curve 3) are presented in Fig. 6. In Fig. 6 the similarity of Curves 1 and 2 and of Curve 3 is seen clearly. In all cases a shift of the absorption maximum toward the long-wave part of the spectrum was observed, which is characteristic of the carbonyl group. The maximum at 302 mμ, ε 13,586 (Curve 1) corresponds to Substance IV, that at 302 mμ , ε 12,792 (Curve 2) to Substance V, and that at 294 mμ , ε 19,604 (Curve 3) to 2-methyl-5-phenylpenten - 4-ol-2-one-3.

In Fig. 7 the absorption curve of the saturated keto alcohol, 2-methyl-5,5-diphenylpentanol-2-one-3 (Substance VIII), is given, which differs sharply from the curves presented in Fig. 6.

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* The ultraviolet spectra were taken by T. N. Naugolnaya and Z. A. Dranitskaya, to whom we express our appreciation.

EXPERIMENTAL

The substance with a m. p. of 132-133° was obtained in a yield of 93% as light-greenish, fine, acicular crystals with a m. p. of 132-133° (from alcohol), according to a method described earlier [1], by the action of a 7.5% alcoholic solution of sulfuric acid on a symmetrical dimethyldiphenylbutynediol.

Determination of the Number of Hydroxyl Groups by Terentyev's Method

0.0857 g sub.: 7.4 ml CH_4 (17°, 750 mm). 0.0461 g sub.: 4.0 ml CH_4 (13°, 774 mm). Found %: OH 5.94, 6.26; number of OH-groups: 0.93, 0.98. $C_{18}H_{17}O(OH)$. Calculated %: OH 6.39; number of OH-groups 1.0.

1. The reaction of the substance with a m. p. of 132-133° with 2,4-dinitrophenylhydrazine was carried out exactly according to the procedure of [5], but because of the poor solubility of the substance in alcohol, one and one-half times the quantity of alcohol was used. After 30-40 minutes a bright-red turbidity appeared, and after 24 hours a bright-red precipitate came down, which was filtered off, washed with 60% alcohol and dried in the air. The fine crystals were very soluble in hot alcohol; their m. p. was 202° (decomp.) The substance gave the pyrazoline reaction.

0.0950 g sub.: 0.2236 g CO_2; 0.0454 g H_2O. 0.0951 g sub.: 0.2234 g CO_2; 0.0456 g H_2O. 4.89 mg sub.: 0.524 ml N_2 (22°, 771 mm). 4.28 mg sub.: 0.465 ml N_2 (23.5°, 772 mm). Found %: C 64.19, 64.07; H 5.31, 5.33; N 12.58, 12.70. $C_{24}H_{22}O_3N_4$(Pyrazoline of the unsaturated keto alcohol). Calculated %: C 64.58; H 4.93; N 12.56. $C_{30}H_{26}O_8N_8$ (Dinitrophenylosozone of the diketone). Calculated %: C 57.51; H 4.15; N 17.88.

According to analytical data, the reaction product of the substance with a m. p. of 132-133° corresponded to the substituted pyrazoline of the unsaturated α-keto alcohol.

2. Action of hydroxylamine on the substance with a m. p. of 132-133°. The experiment described in [1] was repeated, i.e., continued heating of an alcoholic solution of the substance, with hydroxylamine and 2 drops of concentrated hydrochloric acid.* On heating, the solution darkened strongly; after removal of the alcohol a very small quantity of a substance which contained nitrogen (qualitative test) was formed, and after careful purification it melted in the range of 133-142° (decomp.) On heating this substance with a 5% solution of hydrochloric acid for the purpose of hydrolysis, we were unable to separate any individual product, because of resinification.

3. Production of the acetate for the substance with a m. p. of 132-133°. (The acetate of 2-methyl-5,5-diphenylpentene-4-ol-2-one-3). A mixture of 2 g of the substance with a m. p. of 132-133°, 2 g of fused sodium acetate and 8 ml of freshly-distilled acetic anhydride was heated at a slight boil for 5 hours.

After cooling, the solidified substance was diluted with water and partially neutralized with soda. The heavy oil which separated was extracted with ether, the ether extract was washed with a soda solution and with water, and dried with sodium sulfate. After removal of the ether, coarse, colorless crystals were separated, which after several recrystallizations from alcohol had a m. p. of 72-75°.

The resulting product was highly soluble in the usual organic solvents. The reaction for hydroxyl and carbonyl groups was negative. The substance reacted with bromide in chloroform and with potassium permanganate.

11.13 mg sub.: 31.72 mg CO_2; 6.76 mg H_2O. 9.90 mg sub.: 28.32 mg CO_2; 6.15 mg H_2O; 0.1621 g sub.: 16.86 g benzene: Δt 0.16°. 0.2875 g sub.: 0.98 ml 1 N alcoholic solution NaOH. Found %: C 78.78, 78.06; H 6.79, 6.81; M 305.7; saponification equivalent 295.5; % $COCH_3$ 14.54. $C_{20}H_{20}O_3$. Calculated %: C 77.92; H 6.49; M 308; saponification equivalent 308; % $COCH_3$ 13.96.

After hydrolysis of the ester by alcoholic alkali, from the acidified solution a substance with a m. p. of 132-133° separated.

Analytical data showed that the reaction product with a m. p. of 72-73° corresponded to the acetate of the ethylenic α-keto alcohol.

4. Ozonization of the substance with a m. p. of 132-133°. The ozonide, obtained from 2 g of the substance dissolved in 35 ml of chloroform, was decomposed by heating; after addition of several deops of hydrogen peroxide and neutralization of the acids, the neutral products were steam-distilled. 0.28 g of benzophenone with a m. p. of 48° and traces of acetone (reaction with 2,4-dinitrophenylhydrazine and sodium nitroprusside) were found. Benzophenone was also formed in a quantity of 0.82 g from the neutral products, which were non-volatile with steam, and was characterized by a semicarbazone with a m. p. of 164°, which gave no melting point depression with the

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* In [1] [J. Gen. Chem., 20, 2227 (1950)] there was a misprint: instead of sulfuric acid it should read hydrochloric acid.

semicarbazone of known benzophenone. The total yield of benzophenone was 80%.

The acidic ozonization products contained α-hydroxyisobutyric acid, which was non-volatile with steam, and a negligible quantity of benzoic and formic acids, which were separated from the hydroxyisobutyric acid by steam-distillation. After evaporation of the ether, the hydroxybutyric acid, in a quantity of 0.42 g (54%) was obtained as a viscous oil which rapidly crystallized. The acid, purified on a porous plate and also by sublimation, had a m. p. of 76.5-78°; no melting point depression was detected in a mixture with known hydroxyisobutyric acid.

0.1929 g sub.: 19.6 ml 0.1 N NaOH. Found: equivalent 98.4. $C_4H_8O_3$. Calculated equivalent 104.

Because of its decomposition with severe blackening, we were unable to analyze the silver salt obtained from the ammonium salt of hydroxybutyric acid and silver nitrate.

The chief ozonization products, benzophenone (80%) and α-hydroxyisobutyric acid (54%), confirmed the assumed structure of the substance with a m. p. of 132-133°, as the ethylenic α-keto alcohol.

Traces of acetone, and formic and benzoic acids were probably formed as a consequence of the partial decomposition of the chief ozonization products.

5. Hydrogenation of the substance with a m. p. of 132-133°. (Production of 2-methyl-5,5-diphenylpentanol-2-one-3). The hydrogenation was carried out in ethyl acetate with a colloidal palladium catalyst. 2.66 g of the substance with a m. p. of 132-133°, 60 ml of ethyl acetate, and at first 5 ml of colloidal palladium (4.5 mg Pd) were used. Catalyst had to be added several times, since the hydrogenation slowed down rather quickly. In all, 12 ml of catalyst was used. The slowly-occurring hydrogenation was carried out until disappearance of the greenish color of the solution; moreover, somewhat more hydrogen was absorbed than was required for one double bond.

After cessation of the hydrogenation the catalyst was filtered off, and the solution of the substance in ethyl acetate was removed from the aqueous layer, and dried with sodium sulfate. The residue quickly recrystallized after removal of the solvent. Purification was carried out by washing the substance on a porous plate with hexane, and recrystallization from a mixture of petroleum and ethyl ethers (1:1). Fine, colorless needles, cohering in clusters, were obtained. The m. p. was 66-67°. The yield was 2.2 g (81.8%).

The substance was highly soluble in the usual organic solvents, besides petroleum ether; it reacted energetically with methylmagnesium iodide, and liberated methane; it did not decolorize a solution of bromide in chloroform, but reacted very sluggishly with potassium permanganate.

7.58 mg sub.: 22.33 mg CO_2; 5.13 mg H_2O. 13.52 mg sub.: 39.86 mg CO_2; 9.31 mg H_2O. 0.0317 g sub.: 2.8 ml CH_4 (18°, 757 mm). 0.0501 g sub.: 4.7 ml CH_4 (18°, 757 mm). 0.1400 g sub.: 11.60 g benzene: Δt 0.22°. Found %: C 80.34, 80.41; H 7.57, 7.70; OH 6.25; 6.52; M 274. $C_{18}H_{19}O(OH)$. Calculated %: C 80.60; H 7.46; OH 6.34; M 268.

The 2,4-dinitrophenylhydrazone precipitated rather rapidly on pouring together an alcoholic solution of the substance and an alcoholic solution of 2,4-dinitrophenylhydrazine [5]. After several recrystallizations from boiling ethyl alcohol the m. p. was 208-209°.

0.0909 g sub.: 0.2133 g CO_2; 0.0450 g H_2O. 0.1021 g sub.: 0.2397 g CO_2; 0.0504 g H_2O. 7.42 mg sub.: 0.794 ml N_2 (22°, 766 mm). 7.41 mg sub.: 0.801 ml N_2 (21°, 761 mm), Found %: C 63.99, 64.03; H 5.50, 5.48; N 12.40, 12.54. $C_{24}H_{24}O_5N_4$. Calculated %: C 64.29, 5.36; N 12.50.

According to its properties and to analytical data the substance with a m. p. of 66-67° was the saturated α-keto alcohol.

Oxidation of the substance with a m. p. of 66° by lead tetraacetate. Essentially the oxidation was carried out under the conditions cited in the literature [6], with a few modifications. 1.4 g of the substance with a m. p. of 66-67°, 3 g of lead tetraacetate (29% excess), and 40 ml of 90% CH_3COOH were mixed in a two-necked flask with a mercury seal and a highly efficient reflux condenser. No appreciable evolution of heat was observed. After an hour of stirring, it was heated for 1 hour at 50-60°, also with stirring. It was cooled, diluted with 50 ml of water, and the volatile oxidation products were removed by heating in an alcoholic solution of 2,4-dinitrophenylhydrazine. A yellow precipitate came down at once. Removal was continued until a negative test with a 2,4-dinitrophenylhydrazine solution was obtained. The dinitrophenylhydrazone precipitate was filtered off, washed with water, and recrystallized from alcohol. It consisted of fine, yellow needles with a m. p. of 125-126°; a test of a mixture with the known 2,4-dinitrophenylhydrazone of acetone produced no melting point depression. 0.83 g of the dinitrophenylhydrazone, which corresponded to 0.2 g of acetone (68%), was obtained.

After removal of the acetone the residue in the flask was acidified with dilute hydrochloric acid, the lead chloride was filtered off, washed with ether, and an ether extraction was made from the solution. The residue began to crystallize after drying by sodium sulfate and removal of the ether. A portion of the substance was transferred to a porous plate for removal of the residuals of acetic acid; a portion was dissolved in alkali, and on acidification of the solution with dilute sulfuric acid a solid separated. In both cases an acid with a m. p. of 138-142° was obtained. After recrystallization from a mixture of ether and petroleum ether (b. p. 75-90°)(1:2) 0.88 g (74%) of a substance with a m. p. of 148-149° was obtained.

0.1901 g sub.: 8.7 ml 0.1 N NaOH. Found: equivalent 220.9. $C_{15}H_{14}O_2$. Calculated: equivalent 226.

A portion of the acid was converted, via the ammonium salt, to the silver salt, which was analyzed.

0.1178 g sub.: 0.2323 g CO_2; 0.0427 g H_2O; 0.0380 g Ag. 0.0802 g sub.: 0.1581 g CO_2; 0.0289 g H_2O; 0.0258 g Ag. Found %: C 53.78, 53.75; H 4.05, 4.00; Ag 32.26, 32.17. $C_{15}H_{13}O_2Ag$. Calculated %: C 54.05; H 3.90; Ag 32.43.

The analytical data and the properties of the acid corresponded to β,β-diphenylpropionic acid [7], and consequently, the saturated α-keto alcohol was 2-methyl-5,5-diphenylpentanol-2-one-3.

6. Action of 20% sulfuric acid on 2-methyl-5,5-diphenylpentene-4-ol-2-one-3. 2.5 g of the substance with a m. p. of 132-133° and 30 ml of a 20% alcoholic solution of sulfuric acid (H_2SO_4 92%, alcohol 95%) were heated at 65-70° for 5 hours with continuous stirring. On completion of the heating, the color of the solution had almost disappeared. Separation of the reaction product was as usual [1]. A portion of the substance was recrystallized from 95% alcohol, and a portion was recrystallized from petroleum ether; its m. p. was 65-66°. In a mixture with 2,2-dimethyl-5,5-diphenyltetrahydrofuranone-3 no melting point depression was observed, but in a mixture with the original substance there was a sharp depression to 54-58°. The semicarbazone separated very rapidly and melted at 210°. In a mixture with the semicarbazone of tetrahydrofuranone no melting point depression occurred, but with the semicarbazone of the original substance a strong depression occurred.

The tetrahydrofuranone yield was 2.3 g (92%).

SUMMARY

1. It was established that the substance with a m. p. of 132-133°, which formed as a result of the isomerization of asymmetrical dimethyldiphenylbutynediol (2-methyl-5,5-diphenylpentyne-3-diol-2,5), under the influence of a 7.5% alcoholic solution of sulfuric acid, had the structure of the ethylenic α-keto alcohol, 2-methyl-5,5-diphenylpentene-4-ol-2-one-3, and not of the diketone, 2-methyl-5,5-diphenylpentanedione-3,4.

2. An ozonization of this keto alcohol was carried out; the acetate of the keto alcohol, not described in the literature, was obtained.

3. It was shown that the corresponding saturated α-keto alcohol, 2-methyl-5,5-diphenylpentanol-2-one-3, not described in the literature, formed on catalytic reduction of the ethylenic α-keto alcohol.

4. It was observed that, under the influence of a 20% alcoholic solution of sulfuric acid, the ethylenic α-keto alcohol isomerized to 2,2-dimethyl-5,5-diphenyltetrahydrofuranone-3.

5. A mechanism of the isomerization of 2-methyl-5,5-diphenylpentyne-3-diol-2,5 to the ethylenic α-keto alcohol and to tetrahydrofuranone was proposed.

6. The structure of the unsaturated and saturated α-keto alcohols was confirmed by investigation of their infrared and ultraviolet spectra.

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TERTIARY TRIATOMIC ALCOHOLS OF THE ACETYLENE SERIES AND THEIR TRANSFORMATIONS

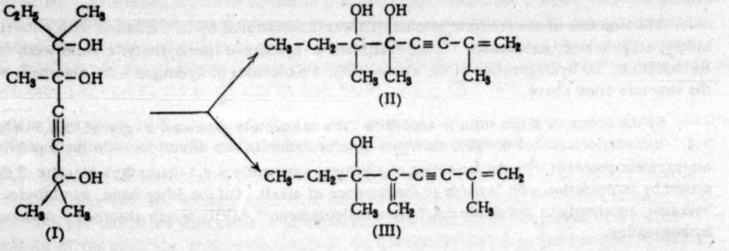
V. DEHYDRATION OF 3,4,7-TRIMETHYLOCTYNE-5-TRIOL-3,4,7

V. I. Nikitin and A. Kh. Khamatov

In a previous report [1] we described the dehydration of 2,3,6-trimethylheptyne-4-triol-2,3,6 by the action on the latter of 20% sulfuric acid, potassium bisulfate or p-toluenesulfo acid. It was shown that the reaction proceeds chiefly with the formation of an α-glycol of the vinylacetylene series, trimethylisopropenylacetylenylethylene glycol. The dehydration of the triol, with the liberation of two molecules of water and the formation of a dienyne carbinol, 2,6-dimethylmethylene-3-pentyne-4-ene-6-ol-2, occurred simultaneously with this to a smaller extent.

In the present report are presented results which we obtained in a study of the action of dehydrating agents on 3,4,7-trimethyloctyne-5-triol-3,4,7 (I), which one of us synthesized for the first time [2] and which is apparently the next homolog of trimethylheptynetriol.

3,4,7-Trimethyloctyne-5-triol-3,4,7 (I) was subjected to the action of 20% sulfuric acid and potassium bisulfate, for which in both cases the chief reaction product was an α-glycol, dimethylethylisopropenylacetylenylethylene glycol (3,4,7-trimethyloctene-7-yne-5-diol-3,4) (II) with a m. p. of 51-52°. The dienyne carbinol, 3,7-dimethyl-4-methyleneoctene-7-yne-5-ol-3 (III), was also always obtained in a small quantity of about 6-8%. A mobile liquid of pleasant odor, and a b. p. of 84-85° (7 mm), it readily polymerized to a dark-red, viscous substance.

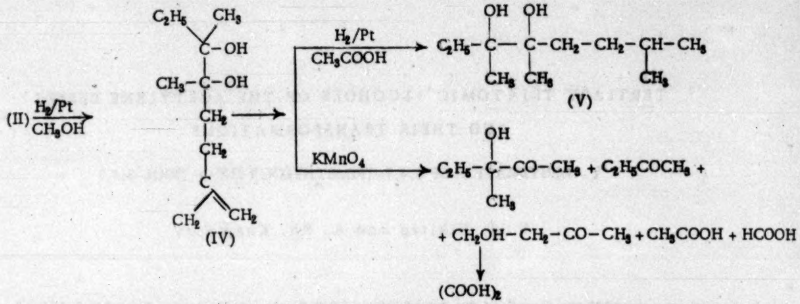


However, it should be noted that on dehydration of the triol by 20% sulfuric acid, a considerable portion of it resinified, as a consequence of which the yield of the vinylacetylene glycol (II) did not exceed 23%. On vacuum distillation of the same triol over potassium bisulfate at 3-4 mm at a bath temperature of 150-155°, the glycol (II) yield reached 70%.

The structure of the glycol (II) was demonstrated by its oxidation with potassium permanganate; moreover, methyl ethyl ketone, methylethylacetylcarbinol, and formic, acetic and oxalic acids were obtained.

Hydrogenation of the glycol (II) in the presence of a platinum catalyst, in a solution of anhydrous methanol, took place vigorously, but after the addition of two molecules of hydrogen it almost ceased. The ethylenic glycol (IV) obtained at this time boiled at 85-86° (1.5 mm).

Methyl ethyl ketone, methylethylacetylcarbinol, butanol-1-one-3 and formic, acetic and oxalic acids were formed by the oxidation of the ethylenic glycol with potassium permanganate. It can be assumed that the oxalic acid formed as a result of further oxidation of the butanol-1-one-3.

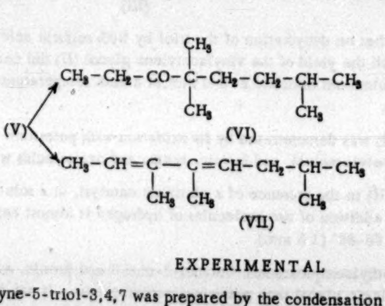


Zalkind and his coworkers [3], and Nazarov and Fischer [4] found that the vinylacetylene series alcohols are readily hydrogenated to the saturated alcohols. At first hydrogenation proceeds at the triple bond until formation of the dienic carbinol, after which further addition of hydrogen is directed to different positions of the conjugated system 1, 2; 3, 4 and 1, 4; $-\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}H_2$. If hydrogenation ceases after 4 atoms of hydrogen per molecule of the vinylacetylene alcohol are added, then the hydrogenation products are a mixture either of two of the isomeric ethylenic alcohols [3], or of all of the three which are possible [4].

In accordance with this, the formation of three isomeric α-glycols can be expected on hydrogenation of 3,4,7-trimethyloctene-7-yne-diol-3,4 (II). However, on oxidation of the α-glycol which we obtained we separated formic acid, but to all intents and purposes did not observe acetone or isobutyric acid in the oxidation products, which would indicate the addition of hydrogen in the 1,4 or 3,4 position. This condition, and also the formation of other oxidation products corresponding to the glycol, enabled us to assign to the glycol with a b. p. of 85-86° (1.5 mm) the structure of 3,4,7-trimethyloctene-7-diol-3,4 (IV). In glacial acetic acid with the absorption of 1 molecule of hydrogen, the ethylenic glycol (IV) hydrogenates further to the completely saturated glycol, 3,4,7-trimethyloctanediol-3,4 (V).

The structure of the dienynic alcohol (III) was demonstrated by its oxidation with potassium permanganate. Methyl ethyl ketone, and formic, acetic, oxalic and α-hydroxy-α-methylbutyric acids were formed as a result of its oxidation. On hydrogenation of the alcohol (III), 4 molecules of hydrogen were absorbed, which also confirms the structure cited above.

By the action of dilute sulfuric acid (20%) the completely saturated α-glycol, 3,4,7-trimethyloctanediol-3,4,7-trimethyloctanediol-3,4 (V), undergoes transformation in two directions. On the one hand, the pinacoline rearrangement proceeds with the formation of a ketone, apparently 4,4,7-trimethyloctanone-3 (VI); an acid is obtained by its oxidation with bromine in the presence of alkali. On the other hand, trimethyloctanediol (V) was dehydrated, apparently to the dienic 3,4,7-trimethyloctadiene-2,4 (VII), which absorbed 2 molecules of hydrogen on hydrogenation.



EXPERIMENTAL

3,4,7-Trimethyloctyne-5-triol-3,4,7 was prepared by the condensation of dimethylacetylenylcarbinol and methylethylacetylcarbinol by a method described in [2].

B. p. 118-119° (2 mm), d_4^{20} 1.0239, n_D^{20} 1.4796, MR_D 55.45.

I. Dehydration of 3,4,7-Trimethyloctyne-5-triol-3,4,7. Sulfuric acid. A mixture of 13.5 g of 3,4,7-trimethyloctyne-5-triol-3,4,7 and 100 ml of 20% sulfuric acid was heated on a boiling water bath for 30 minutes. The dark-red, oily product which separated was extracted with ether, treated with a dilute soda solution, dried with sodium sulfate, and after removal of the ether was vacuum distilled at 1.5 mm. The following fractions were obtained: 1st fraction, 47-51°, 1.8 g, n_D^{20} 1.4890; 2nd fraction, 72-76°, 3.1 g (23%), crystals with a m. p. of 51-52°; 3rd fraction, 110-114°, n_D^{20} 1.4738 – unreacted 3,4,7-trimethyloctyne-5-triol-3,4,7; a resinified residue, 4.5 g.

Potassium bisulfate. 23.1 g of 3,4,7-trimethyloctyne-5-triol-3,4,7, 7 g of finely pulverized potassium bisulfate and 0.1 g of pyrogallol were placed in a Favorsky flask. The mixture was heated on the bath at 150-155° in vacuo at 3-5 mm. 18.1 g (86%) of a substance distilled at 80-110°. In all, 166.5 g of the triol was dehydrated with potassium bisulfate (in separate portions of 20-25 g), and 139.2 g of dehydration products was obtained.

The crude reaction product was dissolved in ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled: 1st fraction, 78-80° (7 mm), 11.6 g, n_D^{20} 1.4951; 2nd fraction, 80-83° (2 mm), 96.4 g, crystals with a m. p. of 51-52°; 3rd fraction, 110-115° (2 mm), 17.2 g n_D^{20} 1.4750 – unreacted 3,4,7-trimethyloctyne-5-triol-3,4,7.

The crystals dissolved well in the usual solvents, but we were able to recrystallize it from none of the solvents.

Similar fractions from all the experiments were combined and vacuum distilled. Two fractions were separated after several distillations: 1st, 84-85° (7 mm), n_D^{20} 1.5015 – 3,7-dimethyl-4-methyleneoctene-7-yne-5-ol-3 (III); 2nd, 80-82° (2 mm), crystals with a m. p. of 51-52°, apparently 3,4,7-trimethyloctene-7-yne-5-diol-3,4 (II).

Investigation of the Fraction with a B. p. of 84-85° (7 mm).

d_4^{20} 0.9061, n_D^{20} 1.5015, MR_D 53.37. $C_{11}H_{16}O$. Calc. 51.59.

0.1324 g sub.: 0.3894 g CO_2; 0.1196 g H_2O. 0.1028 g sub.: 16.4 ml CH_4 (22°, 688.2 mm). 0.1576 g sub.: 27 ml CH_4 (23.5°, 688.2 mm). Found %: C 80.20; H 10.06; OH 10.17, 10.86. $C_{11}H_{16}O$. Calculated %: C 80.43; H 9.83, OH 10.3.

Oxidation. 16.6 g of the substance in 100 ml of water was used. 500 ml of the 4% solution of potassium permanganate was added dropwise during 3 hours with stirring by a mechanical stirrer, and 76 g more of finely ground potassium permanganate (96 g of $KMnO_4$ from calculation of 9 active oxygen atoms per 1 molecule of the alcohol oxidized) was introduced in small portions during 6 hours. On completion of the oxidation the manganese dioxide was filtered off, and from the filtrate a distillate of neutral substances was removed. After saturation by sodium sulfate 250 ml of the distillate of neutral substances was distilled, and from the latter two fractions were separated by a fractionation column: 1st, 67-71°, 0.6 g, n_D^{20} 1.3878; 2nd, 71-80°, 0.8 g, n_D^{20} 1.3840.

A 2,4-dinitrophenylhydrazone with a m. p. of 113-114° was obtained from both fractions. A test of a mixture with the 2,4-dinitrophenylhydrazone of known methyl ethyl ketone showed no depression.

After removal of the neutral substances the solution was acidified with hydrochloric acid, and the volatile acids were steam-distilled. The distilled volatile acids were neutralized and evaporated to a small volume, acidified with hydrochloric acid and extracted with ether in an extractor. The ether extract was dried with sodium sulfate, and after removal of the ether the acids were distilled: 1st fraction, 90-95°, 2 g; 2nd fraction, 95-110.0°, 5 g; 3rd fraction, 110-115°, 3.1 g.

The 1st fraction was formic acid, which gave calomel with mercuric chloride. The 3rd fraction was acetic acid, which was established by the cacodyl test and by an analysis of the silver salt.

0.0786 g salt: 0.0706 g Ag. 0.0804 g salt: 0.0516 g Ag. Found %: Ag 64.30, 64.17. CH_3COOAg. Calculated %: Ag 64.65.

The solution which remained after removal of the volatile acids was neutralized with alkali, and oxalic acid was precipitated by the action of $CaCl_2$. The calcium salt precipitate was filtered off, dissolved in hydrochloric acid and extracted with ether in an extractor. After removal of the ether 4.1 g of oxalic acid was obtained. Its m. p. was 101-102° (test of a mixture).

After precipitation of the calcium salt the filtrate was acidified with hydrochloric acid and treated with ether. After removal of the ether, 0.5 g of α-hydroxy-α-methylbutyric acid with a m. p. of 71-72° (from a mixture of petroleum ether and benzene) was obtained from the ether extract [5]. A test sample of a mixture with the form of α-hydroxy-α-methylbutyric acid obtained by oxidation of 3,6,7-trimethyloctyne-4-triol-3,6,7 produced no melting point depression.

Thus, methyl ethyl ketone, formic, acetic, oxalic and α-hydroxy-α-methylbutyric acids were obtained as a result of the oxidation of the fraction with a b. p. of 84-85° (7 mm), n_D^{20} 1.5015.

Hydrogenation of 3,7-Dimethyl-4-methyleneoctene-7-yne-5-ol-3. 7.8 g of the substance in a solution of 75 ml of dry methanol was hydrogenated over platinum oxide (according to Adams) for 8 hours. 4600 ml of hydrogen (22°, 690.4 mm) was absorbed. 4760 ml of hydrogen was calculated for 4 moles.

After removal of the methanol the hydrogenation product was vacuum distilled. A fraction with a b. p. of 78-79° (7 mm), apparently 3,4,7-trimethyloctanol-3, was separated.

d_4^{20} 0.8536, n_D^{20} 1.4770, MR_D 53.84. $C_{11}H_{24}O$. Calc. 54.52.

0.1346 g sub.: 0.3784 g CO_2; 0.1703 g H_2O. 0.1622 g sub.: 0.4542 g CO_2; 0.2004 g H_2O. Found %: C 76.68; 76.38; H 13.90, 13.82. $C_{11}H_{24}O$. Calculated %: C 76.65; H 14.05.

Investigation of the Fraction with a B. p. of 80-82° (2 mm), M. p. 51-52°.

0.1666 g sub.: 0.4418 g CO_2; 0.1462 g H_2O. 0.1468 g sub.: 0.3904 g CO_2; 0.1332 g H_2O. 0.1012 g sub.: 29.2 ml CH_4 (17.5°, 696.4 mm). 0.0987 g sub.: 27.9 ml CH_4 (18°, 696.4 mm). Found %: C 72.31, 72.52; H 9.82, 10.15; OH 18.73, 18.48. $C_{11}H_{18}O_2$. Calculated %: C 72.46; H 9.96; OH 18.68.

Oxidation. 18.3 g of the substance in 100 ml of water was placed in a flask equipped with a mechanical stirrer, and 1600 ml of a 4% solution of potassium permanganate (64 g of $KMnO_4$) was added dropwise during 10 hours, with vigorous stirring.

Further investigation of the oxidation products was carried out as in the preceding experiment, as a result of which methyl ethyl ketone and methylethylacetylcarbinol was separated from the neutral products.

Methyl ethyl ketone boiled at 75-80° (1.5 g), its 2,4-dinitrophenylhydrazone melted at 113-114°, and it produced no melting point depression of a test sample of a mixture with the 2,4-dinitrophenylhydrazone of known methyl ethyl ketone. The semicarbazone had a m. p. of 146-147°, which corresponded to the semicarbazone of methyl ethyl ketone (test of a mixture).

Methylethylacetylcarbinol had a b. p. of 147-149° (698.4 mm), n_D^{20} 1.4220. Its 2,4-dinitrophenylhydrazone, with a m. p. of 107-108°, produced no melting point lowering of a test sample of a mixture with the 2,4-dinitrophenylhydrazone of known methylethylacetylcarbinol.

Of the acids the following were obtained: formic, acetic (4.4 g), and oxalic (3.2 g) with a m. p. of 101-102° (test of a mixture).

The presence of the first two acids was established by the calomel and cacodyl tests, and by obtaining the silver salt for acetic acid.

0.1042 g salt: 0.0674 g Ag. 0.0956 g salt: 0.0614 g Ag. Found %: Ag 64.71, 64.22. CH_3COOAg. Calculated %: Ag 64.65.

Thus, methyl ethyl ketone, methylethylacetylcarbinol and formic, acetic and oxalic acids were obtained by oxidation of the crystalline substance with a m. p. of 51-52°.

Hydrogenation of 3,4,7-trimethyloctene-7-yne-5-diol-3,4 in a methanol solution. 13.75 g of the substance in 70 ml of dry methanol was hydrogenated over platinum oxide. 4 liters of hydrogen (21°, 692 mm) was absorbed in 5 hours. Hydrogenation almost ceased after the addition of 4 liters of hydrogen (2 moles). The reaction products were vacuum distilled. 10.5 g of the substance, 3,4,7-trimethyloctene-7-diol-3,4 (IV), was separated.

B. p. 85-86° (1.5 mm), d_4^{20} 0.9337, n_D^{20} 1.4645, MR_D 55.01. $C_{11}H_{22}O_2$. Calc. 55.58.

0.1320 g sub.: 0.3412 g CO_2; 0.1472 g H_2O. 0.0898 g sub.: 0.2328 g CO_2; 0.1000 g H_2O. 0.1569 g sub.: 43.4 ml CH_4 (26.5°, 687.6 mm). 0.1068 g sub.: 29.8 ml CH_4 (26°, 687.6 mm). Found %: C 70.50, 70.69; H 12.47, 12.46; OH 17.06, 17.53. $C_{11}H_{22}O_2$. Calculated %: C 70.90; H 11.91; OH 18.27.

Oxidation of 3,4,7-trimethyloctene-7-diol-3,4. 670 ml of a 2% solution of potassium permanganate was slowly introduced during 6 hours into 7.7 g of the substance in 100 ml of water, with stirring by a mechanical stirrer. Investigation of the oxidation products was carried out similarly to the preceding oxidations.

Methyl ethyl ketone (0.8 g) and methylethylacetylcarbinol (1.2 g), which were identified by obtaining their 2,4-dinitrophenylhydrazones, were separated from the neutral substances. Moreover, about 0.5 g of a substance separated, the 2,4-dinitrophenylhydrazone of which melted at 142-143° (from ethyl alcohol).

3.880 ml sub.: 0.730 ml N_2 (22°, 741 mm). 3.970 mg sub.: 0.740 ml N_2 (22°, 741 mm). Found %: N 21.15, 20.96. $C_{10}H_{12}O_5N_4$. Calculated %: N 21.0.

We were unable to carry out any other investigations for this substance, because of its small quantity; but, judging by the analytical data presented above for nitrogen, it can be assumed that it corresponds to butanol-1-one-3.

The solution of the salts, after removal of the neutral substances from it, was acidified with hydrochloric acid, and from it 570 ml of a volatile acid distillate was steam-distilled, for the neutralization of which 237 ml of 0.1 N NaOH was consumed. The presence of formic and acetic acids was established by the calomel and cacodyl tests. 0.5 g of oxalic acid was obtained (test of a mixture) from the non-volatile acids by extraction with ether in an extractor.

Hydrogenation of 3,4,7-trimethyloctene-7-diol-3,4 in acetic acid solution. In the presence of a Pt-catalyst, 6.5 g of the substance [b. p. 85-86° (1.5 mm), n_D^{20} 1.4645] in a solution of 40 ml of glacial acetic acid absorbed 750 ml of hydrogen (800 ml was required for 1 mole of the substance according to calculation). After removal of the methanol the hydrogenation products were distilled, and 4 g of a substance with a b. p. of 107-108° (3 mm), apparently 3,4,7-trimethyloctanediol-3,4 (V), was extracted.

d_4^{20} 0.9220, n_D^{20} 1.4550, MR_D 55.34. $C_{11}H_{24}O_2$. Calc. 56.00.

0.1257 g sub.: 0.3243 g CO_2; 0.1453 g H_2O; 0.1381 g sub.: 0.3574 g CO_2; 0.1577 g H_2O. 0.1347 g sub.: 41.4 ml CH_4 (22.2°, 695.8 mm). 0.1510 g sub.: 44.8 ml CH_4 (27°, 690.1 mm). Found %: C 70.36, 70.68; H 12.53, 12.77; OH 19.79, 18.65. $C_{11}H_{24}O_2$. Calculated %: C 70.23; H 12.85; OH 18.07.

II. Dehydration of 3,4,7-Trimethyloctanediol-3,4 by Sulfuric Acid.

19.2 g of 3,4,7-trimethyloctanediol-3,4 (V) [b. p. 107-108° (3 mm), n_D^{20} 1.4550] was heated with 200 ml of 20% sulfuric acid at 80-90° for 4 hours, with vigorous stirring by a mechanical stirrer.

The reaction products were extracted with ether, neutralized with soda, dried with potash, and after removal of the ether were vacuum distilled. 2 fractions were separated as a result of several distillations at 38 mm: 1st, 97-98°, 5.3 g, apparently the dienic hydrocarbon, 3,4,7-trimethyloctadiene-2,4 (VII); 2nd, 110-112°, 11.62 g, obviously 4,4,7-trimethyloctanone-3 (VI).

Investigation of the Fraction with a B. p. of 97-98° (38 mm)

d_4^{20} 0.8212, n_D^{20} 1.4587, MR_D 50.58. $C_{11}H_{20}$. Calc. 52.06.

0.1300 g sub.: 0.4131 g CO_2; 0.1540 g H_2O. Found %: C 86.68; H 13.25. $C_{11}H_{20}$. Calculated %: C 86.84; H 13.16.

In this fraction the hydroxyl and carbonyl groups were absent.

Hydrogenation. 0.370 g of the substance in a solution of 40 ml of dry methanol was hydrogenated over platinum oxide (according to Adams) for 4 hours. 140 ml of hydrogen was absorbed (27.5°, 688 mm). 135.7 ml of hydrogen for 2 moles was calculated.

Investigation of the Fraction with a B. p. of 110-111° (38 mm)

d_4^{20} 0.8398, n_D^{20} 1.4360, MR_D 52.98. $C_{11}H_{22}O$. Calc. 53.01.

0.1646 g sub.: 0.4647 g CO_2; 0.1898 g H_2O. 0.1288 g sub.: 0.3649 g CO_2; 0.1470 g H_2O. Found %: C 77.49, 77.25; H 12.90, 12.76. $C_{11}H_{22}O$. Calculated %: C 77.56; H 13.03.

A 2,4-dinitrophenylhydrazone with a m. p. of 87-88° was obtained.

6.083 mg sub.: 0.855 ml N_2 (16°, 741 mm). 5.881 mg sub.: 0.840 ml N_2 (22°, 746 mm). Found %: N 15.86, 15.89. $C_{17}H_{26}O_4N_4$. Calculated %: N 16.00.

Oxidation. 5.7 g of substance, 38 g of NaOH and 150 ml of water was introduced into a flask equipped with a mechanical stirrer. 16.1 g of bromine at −10° was slowly introduced dropwise, with vigorous stirring, after which the stirring was continued for 2 more hours. Then the mixture was treated with hyposulfite and the neutral substances were extracted with ether. The ether extract was dried over potash, and after removal of the ether 5 g of crude product was obtained.

4.2 g of a fraction with a b. p. of 110-112° (38 mm), n_D^{20} 1.4324, which was unreacted starting material, was removed by vacuum distillation. After removal of the neutral substances the solution was acidified with hydrochloric acid, and the volatile acids were steam-distilled, neutralized with alkali and evaporated almost to dryness. A silver salt was obtained from the dry residue.

0.0764 g salt: 0.0490 g Ag. Found %: Ag 64.26. CH_3COOAg. Calculated %: Ag 64.65.

The non-volatile acids were extracted with ether in an extractor. After removal of the ether a negligible quantity of a crystalline acid was obtained. The crystals, separated on a porous plate, melted at 93-95°. Because of their small quantity they were not studied closely.

SUMMARY

1. On dehydration of 3,4,7-trimethyloctyne-5-triol-3,4,7, essentially 1 molecule of water split off, by which an α-glycol of the vinylacetylene series formed.

The reaction occurred to a slight extent with the splitting off of 2 molecules of water, as a result of which a certain quantity of the dienynic alcohol formed.

2. On hydrogenation of the vinylacetylene glycol, 3,4,7-trimethyloctene-7-yne-5-diol-3,4, in a methanol solution with a platinum catalyst, only 2 molecules of hydrogen were absorbed and the ethylenic α-glycol, 3,4,7-trimethyloctene-7-diol-3,4, formed.

3. In acetic acid solution in the presence of a platinum catalyst, 3,4,7-trimethyloctene-7-diol-3,4 was hydrogenated to 3,4,7-trimethyloctanediol-3,4.

4. By the action of 20% sulfuric acid, 3,4,7-trimethyloctanediol-3,4 underwent transformation in two directions: on the one hand, the pinacoline rearrangement proceeded with the formation of the ketone, 4,4,7-trimethyl-actanone-3 (chief direction of the reaction); on the other hand, the splitting off of two molecules of water proceeded and the dienic hydrocarbon formed.

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INVESTIGATION IN THE FIELD OF ALKANE SULFO ACIDS

XII. REACTION OF β-CHLOROETHANESULFOCHLORIDE WITH AROMATIC AMINES

A. G. Kostsova, L. S. Shvetsova and I. I. Kalganova

The study of the reaction of β-chloroethanesulfochloride with aromatic amines was the purpose of the present work.

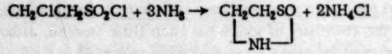
Earlier we described similar reactions with chloromethane- and α-chloroethanesulfochlorides [1]; they showed that chlorine, in the α-position to the SO_2Cl-group, appeared to have rather great stability and had no tendency toward cleavage. The reaction proceeds by the usual order with the formation of the N-arylamides of chloromethane- and α-chloroethanesulfo acids according to the scheme:

$$RCHClSO_2Cl + 2ArNH_2 \rightarrow RCHClSO_2NHAr + ArNH_2 \cdot HCl, \text{ where } R = H \text{ or } CH_3.$$

The chemistry of β-chloroethanesulfochloride has been little studied. However, from the literature it is known that β-chloroethanesulfochloride behaves unusually with respect to some reagents. Thus, with alcohols it gives the esters, not of β-chloroethanesulfo acid, but of vinyl sulfo acid, according to the scheme [2]:

$$CH_2ClCH_2SO_2Cl + ROH \rightarrow CH_2 = CHSO_2OR + 2HCl.$$

It forms the so-called cyclic anhydrotaurine with gaseous ammonia [3]. As with the alcohols, the reaction is accompanied by the splitting off of HCl from the radical. Judging from the literature data, the formation of anhydrotaurine proceeds according to the following equation:



$$CH_2ClCH_2SO_2Cl + 3NH_3 \rightarrow \underbrace{CH_2CH_2SO}_{NH} + 2NH_4Cl$$

Some authors were inclined to assume that this reaction proceeds without the closing of the ring, with formation of the isomeric anhydrotaurine of the amide of vinyl sulfo acid [4].

$$CH_2ClCH_2SO_2Cl + 3NH_3 \rightarrow CH_2 = CHSO_2NH_2 + 2NH_4Cl.$$

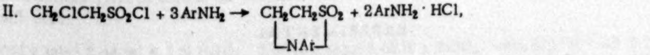
The latter assumption is the most likely, since cyclic anhydrotaurine would probably be readily cleaved to taurine, which as a matter of fact was not observed.

The reactions of β-chloroethanesulfochloride with aromatic amines were not described, therefore, it was of interest to study the behavior of chlorine in the β-position to the SO_2Cl-group in reactions of the type mentioned above.

On carrying out the reactions of β-chloroethanesulfochloride with aromatic amines we had in mind first of all to obtain the corresponding derivatives of β-chloroethanesulfo acid, according to the equation:

$$\text{I. } CH_2ClCH_2SO_2Cl + 2ArNH_2 \rightarrow CH_2ClCH_2SO_2NHAr + ArNH_2 \cdot HCl.$$

We proceeded from the fact that all these reactions will take place under very mild temperature conditions (water bath or room temperature), and consequently, the cleavage of HCl will not occur. But, considering the literature data, we also did not exclude the possibility of the formation of N-arylsubstituted anhydrotaurine or of the N-arylamides of vinyl sulfo acid:



$$\text{II. } CH_2ClCH_2SO_2Cl + 3ArNH_2 \rightarrow \underbrace{CH_2CH_2SO_2}_{NAr} + 2ArNH_2 \cdot HCl,$$

$$\text{III. } CH_2ClCH_2SO_2Cl + 3ArNH_2 \rightarrow CH_2 = CHSO_2NHAr + 2ArNH_2 \cdot HCl.$$

The following aromatic amines were used for the reaction: aniline, p-toluidine, p-anisidine, p-phenetidine, and p-nitroaniline; of the heterocyclic amines, α-aminopyridine was used. The reaction with aniline, p-toluidine, p-anisidine and p-phenetidine was carried out in anhydrous ether, that with p-nitroaniline was carried out in pyridine, and that with α-aminopyridine was carried out in dry benzene or acetone.

In all cases compounds were obtained, the chlorine content of which was confirmed by analysis. Consequently, the reaction did not take place according to Scheme I. It could be assumed that it went according to Scheme II, or according to Scheme III. Quantitative analysis gave no possibility of solving this problem, since the reaction products according to both Scheme II and Scheme III had the same qualitative and quantitative compositions. This problem was solved by means of a study of the properties of the compounds obtained. These compounds were similar in properties to the N-arylsulfamides which we described earlier, i.e., they dissolved well in organic solvents and in dilute alkali, were neutral to litmus, and precipitated from alkaline solutions on acidification; they had the capacity to alkylate in alkaline solutions, which was possible only in the presence of a hydrogen or nitrogen atom; finally, with bromine water and potassium permanganate they gave a reaction for a double bond. Not all the properties enumerated were connected with the cyclic structure (Scheme II), but most corresponded to the vinyl sulfo acid derivative (Scheme III).

Thus, we showed that β-chloroethanesulfochloride reacts with aromatic amines just as does 1,2-ethanedisulfochloride, which with aniline forms the anilide of vinyl sulfo acid according to the reaction [5]

$$CH_2SO_2ClCH_2SO_2Cl + 3C_6H_5NH_2 \rightarrow CH_2=CHSO_2NHC_6H_5 + SO_2 + 2C_6H_5NH_2 \cdot HCl.$$

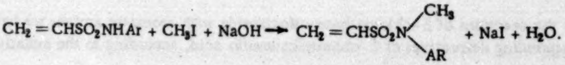
The chlorine in β-chloroethanesulfochloride and the SO_2Cl in 1,2-ethanedisulfochloride are equally unstably bound to the carbon atom, and by the action of aromatic amines are easily split off, together with the mobile α-hydrogen atom, as hydrochloric acid, which at the time of liberation gives a salt with the amines mentioned, and the N-arylamide of vinyl sulfo acid is formed as the chief reaction product.

From these experiments the conclusion follows that the action of aromatic bases on β-chloroethanesulfochloride is similar to the action of an alcoholic alkali solution on the alkyl halides, where the alkali, cutting off the elements of the hydrogen halide, acid from the alkyl halide, leads to formation of ethylene compounds.

As a result of the reactions which we carried out the anilide, p-toluidide, p-anisidide, p-phenetidide, p-nitroanilide and α-aminopyridide of vinyl sulfo acid were obtained and characterized, which considerably extends the data on vinyl sulfo acid derivatives, the chemistry of which has been little studied, although interest in it has increased recently, in connection with its property of forming cation-exchange resins [6].

The resulting compounds were colorless, crystalline, neutral substances (pH 6.9-7.1). They formed in low yields. It is possible that, together with them, the formation of other reaction products which we were unable to separate, also occurs. In any case, the incomplete solution of the crude product was observed on treatment with alkali, and on filtration of the alkaline solution a viscous, gummy, yellow substance remained on the filter.

Some of the compounds obtained were alkylated with methyl iodide in order to demonstrate the presence of a hydrogen atom on the nitrogen. The p-toluidide and p-phenetidide, taken for this purpose, gave well-crystallizing, alkali-insoluble methylation products, N-methyl-p-toluidide and N-methyl-p-phenetidide. Their formation proceeds according to the scheme:



$$CH_2=CHSO_2NHAr + CH_3I + NaOH \rightarrow CH_2=CHSO_2N\begin{matrix} CH_3 \\ AR \end{matrix} + NaI + H_2O.$$

Together with the amines mentioned above, we carried out the reaction of β-chloroethanesulfochloride with p-aminophenol, but except for a viscous, black substance, we were able to separate nothing. With respect to β-chloroethanesulfochloride, p-aminophenol behaves the same as with the 2-methylethane- and phenylmethanesulfochlorides [7], i. e., the whole reaction mixture resinified in this reaction, in spite of employment of the mildest conditions.

Constants of the resulting compounds are recorded in the Table.

EXPERIMENTAL

I. Production of the Starting Materials

The β-chloroethanesulfochloride required for the work was obtained from dichloroethane according to the following scheme:

Test No.	Formula of compound	Name	Melting point	pH
1	$CH_2 = CHSO_2NHC_6H_5$	vinylsulfoanilide	65°	7.38
2	$CH_2 = CHSO_2NHC_6H_4CH_3$	vinylsulfo-p-toluidide	73	7.00
3	$CH_2 = CHSO_2NHC_6H_4OCH_3$	vinylsulfo-p-anisidide	65	6.95
4	$CH_2 = CHSO_2NHC_6H_4OC_2H_5$	vinylsulfo-p-phenetidide	78	7.14
5	$CH_2 = CHSO_2NHC_6H_4NO_2$	vinylsulfo-p-nitroanilide	125	–
6	$CH_2 = CHSO_2NHC_5H_4N$	vinylsulfo-α-aminopyridide	191	6.5
7	$CH_2 = CHSO_2N(CH_3)C_6H_4CH_3$	vinylsulfo-N-methyl-p-toluidide	103 - 105	–
8	$CH_2 = CHSO_2N(CH_3)C_6H_4OC_2H_5$	vinylsulfo-N-methyl-p-phenetidide	67 - 68	–

$$CH_2ClCH_2Cl \xrightarrow{NH_4SCN} CH_2ClCH_2SCN \xrightarrow{2HOH + 3Cl_2} CH_2ClCH_2SO_2Cl.$$

We used this method for the first time (other methods of its production are described in the literature [5, 8]).

Preparation of β-chloroethanethiocyanate. 23.03 g (0.3 mole) of ammonium thiocyanate and 60 ml of anhydrous alcohol were added to 30 g (0.3 mole) of dichloroethane. The reaction flask, equipped with a reflux condenser, was heated at a slight boil for 5-6 hours. Then the mixture was cooled, and the ammonium chloride precipitate which came down was filtered off and washed several times on the filter with small portions of anhydrous alcohol. The alcohol was removed from the filtrate. The residue, consisting of β-chloroethanethiocyanate and 1,2-ethanedithiocyanate, which also formed during this reaction, and ammonium chloride, was treated with water. In addition, the ammonium chloride was dissolved, the dithiocyanate remained insoluble as a solid substance, and the β-chloroethanethiocyanate was emulsified with water. The dithiocyanate was separated, washed on the filter with ether, and the β-chloroethanethiocyanate was extracted from the aqueous emulsion with ether. The ether extract was separated from the water and dried with calcium chloride. After removal of the ether on the water bath, the β-chloroethanethiocyanate which remained was vacuum distilled at 91-92° (15 mm). Its b. p. was 202-203° at atmospheric pressure. The yield of β-chloroethanethiocyanate was 4.1 g (11.14%). It was a colorless, oily liquid with a specific pungent odor. The yield of 1,2-ethanedithiocyanate was 5 g (13.6%). It consisted of colorless, hard crystals with a m. p. of 87-88° and a pungent, obtrusive odor, and it possessed lachrymatory and sternutatory action.

0.1539 g sub.: 12.11 ml 0.1 N H_2SO_4. Found %: N 11.02. C_3H_4NSCl. Calculated %: N 11.52. 0.1000 g sub.: 14.15 ml 0.1 N H_2SO_4. Found %: N 19.81. $C_4H_4N_2S_2$. Calculated %: N 19.44.

Production of β-chloroethanesulfochloride. A strong current of chlorine was passed into an emulsion of 27.3 g of β-chloroethanethiocyanate in 100 ml of water for 4 hours. The reaction temperature was kept at from 0 to 7°. A greenish-yellow oil, β-chloroethanesulfochloride, collected at the bottom of the reaction flask. The oil was separated from the water layer, and washed several times with water, with a weak solution of soda (0.5% solution), and again with water. After separation from the water, it was dried with calcium chloride. The resulting sulfochloride was vacuum distilled at 84-86° (15 mm). According to the literature, its boiling point was 125-127° at 30 mm, and 93-96° at 17 mm [8]. The yield was 23 g (62.7%). It was a mobile liquid with a pungent odor and with lachrymatory action.

II. Reactions of β-Chloroethanesulfochloride with Aromatic Amines

Reaction with aniline, p-toluidine, p-anisidine, p-phenetidine and α-aminopyridine were carried out by a method which we described in previous reports [9]; therefore, a detailed description of it is omitted, and only the most essential experimental data are cited below.

Reaction with aniline. 2 g of β-chloroethanesulfochloride and 3.42 g of freshly-distilled aniline in 15 ml of anhydrous ether were used. The anilide of vinyl sulfo acid which separated crystallized with difficulty, only with strong cooling and rubbing with a glass rod. The yield was 0.9 g (40.6%). The reaction carried out at room temperature gave an anilide yield of 31.2%; the reaction carried out without a solvent gave a yield of 14% of the anilide of vinyl sulfo acid.

0.0644 g sub.: 3.44 ml 0.1 N H_2SO_4. 0.0644 g sub.: 0.0826 g $BaSO_4$. Found %: N 7.48; S 17.67. $C_8H_9O_2NS$. Calculated %: N 7.65; S 17.44.

Reaction with p-toluidine. 2 g of β-chloroethanesulfochloride and 3.9 g of p-toluidine in 35 ml of anhydrous ether were used. The yield of vinylsulfo-p-toluidide was 0.91 g (37.3%). It consisted of colorless crystals which were bitter to the taste. The reaction, carried out without heating, gave a yield of 36.1% of the product. As is evident, the temperature did not affect the yield of vinylsulfo-p-toluidine in the present case.

0.0476 g sub.: 2.41 ml 0.1 N H_2SO_4. 0.0696 g sub.: 0.0842 g $BaSO_4$. Found %: N 7.09; S 16.61. $C_9H_{11}O_2NS$. Calculated %: N 7.10; S 16.24.

Reaction with p-anisidine. 1 g of β-chloroethanesulfochloride and 2.3 g of p-anisidine in 25 ml of anhydrous ether were used. The yield of the product was 0.55 g (42.3%); the yield of vinylsulfo-p-anisidide was 23% at room temperature.

0.052 g sub.: 2.41 ml 0.1 N H_2SO_4. 0.1017 g sub.: 0.1135 g $BaSO_4$. Found %: N 6.51; S 15.32. $C_9H_{11}O_3NS$. Calculated %: N 6.57; S 15.02.

Reaction with p-phenetidine. 2 g of β-chloroethanesulfochloride and 5.4 g of p-phenetidine in 40 ml of anhydrous ether were used. The yield of vinylsulfo-p-phenetidide was 0.7 g (25.9%); the yield was 11.1% at room temperature.

0.0526 g sub.: 2.28 ml 0.1 N H_2SO_4. 0.0578 g sub.: 0.0590 g $BaSO_4$. Found %: N 6.09; S 14.01. $C_{10}H_{13}O_3NS$. Calculated %: N 6.17; S 14.09.

Reaction with p-nitroaniline. 2 g of β-chloroethanesulfochloride was added dropwise to a solution of 1.7 g of p-nitroaniline in 10 ml of pyridine. The mixture was heated on a boiling water bath for 2 hours, and then was left for 1 day. The reaction product, vinylsulfo-p-nitroanilide, together with unreacted p-nitroaniline, was precipitated from the pyridine solution by cold, dilute hydrochloric acid. The dark precipitate which came down was filtered off, and was then treated with dilute alkali with slight heating. After separation of the p-nitroaniline, which did not dissolve in alkali, from the alkaline solution, the vinylsulfo-p-nitroanilide was precipitated by dilute sulfuric acid. The yield was 0.6 g (26.5%). It was a finely-crystalline, yellow power, but the yellow color faded considerably during its purification from alcohol and water. The product differed from the other N-arylamides of vinyl sulfo acid in solubility: it was soluble in alcohol, benzene, and chloroform only on heating, whereas the above-described N-arylsulfoamides dissolved in these solvents in the cold.

0.0809 g sub.: 7.00 ml 0.1 N H_2SO_4. 0.1000 g sub.: 0.1036 g $BaSO_4$. Found %: N 12.12; S 14.23. $C_8H_8O_4N_2S$. Calculated %: N 12.28; S 14.03.

Reaction with α-aminopyridine. 1.5 g of β-chloroethanesulfochloride and 1.73 g of α-aminopyridine in 20 ml of anhydrous benzene were used. The yield of vinylsulfo-α-aminopyridide was 0.2 g (11.8%). Conduction of the reaction in acetone gave results similar to those obtained with benzene. The vinylsulfo-α-aminopyridide consisted of fine, colorless crystals, which were bitter to the taste, highly soluble in water in the cold, highly soluble in alcohol on heating, but insoluble in chloroform, ether, benzene, and dichloroethane. Recrystallization was made from alcohol.

0.0355 g sub.: 3.81 ml 0.1 N H_2SO_4. 0.0301 g sub.: 0.0385 g $BaSO_4$. Found %: N 15.03; S 17.56. $C_7H_8O_2N_2S$. Calculated %: N 15.20; S 17.39.

Methylation of vinylsulfo-p-toluidide. 0.45 g of methyl iodide was added to 0.14 g of vinylsulfo-p-toluidide in a solution of 5% alkali. Conduction of the reaction and isolation of the methylated product were carried out analogously to that which we described earlier [9]. The yield of the vinylsulfo-N-(methyl)-p-toluidide was 0.11 g (73.3%). It was recrystallized from alcohol and water. It consisted of fine, colorless crystals, which were sweet to the taste.

0.0481 g sub.: 2.2 ml 0.1 N H_2SO_4. Found %: N 6.40. $C_{10}H_{13}O_2SN$. Calculated %: N 6.63.

Methylation of vinylsulfo-p-phenetidide. 0.16 g of the p-phenetidide of vinyl sulfo acid in 5% alkali and 0.45 g of CH_3I were used. The yield of vinylsulfo-N-methyl-p-phenetidide was 0.14 g (82.3%). It was recrystallized from alcohol and water.

0.0508 g sub.: 2.04 ml 0.1 N H_2SO_4. Found %: N 5.60. $C_{11}H_{15}O_3NS$. Calculated %: N 5.80.

SUMMARY

1. A method of production of β-chloroethanesulfochloride from dichloroethane was proposed.

2. The reactions of β-chloroethanesulfochloride with the following aromatic amines were studied: aniline, p-toluidine, p-anisidine, p-phenetidine, p-nitroaniline, and also with α-aminopyridine.

3. It was found that chlorine in the β-position to the sulfo-group possesses great mobility, as a result of which the above-mentioned reactions proceed with the cleavage of HCl from the radical, and with the formation of the corresponding N-arylamides of vinyl sulfo acid.

4. The anilide, p-toluidide, p-anisidide, p-phenetidide, p-nitroanilide and α-aminopyridide of vinyl sulfo acid were obtained and characterized.

5. The effect of temperature on the yields of the reaction products was shown.

6. The methylation products of the p-toluidide and p-phenetidide of vinyl sulfo acid, by which the structure of the N-arylsulfamides obtained was demonstrated, were obtained and characterized.

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* T. p. = C. B. Translation pagination.

3. It was found that an increase in the [illegible] of the amino group [illegible], as a result of which [illegible] from the [illegible], and with the formation of the corresponding N-arylamides of [illegible] acid.

4. The anilide, p-toluidide, p-anisidide, p-phenetidide, p-nitroanilide and [illegible] of [illegible] acid [illegible] and characterized.

5. The effect of temperature on the yields of the reaction products was shown.

6. The hydrolysis products of the p-toluidide and p-phenetidide of [illegible] acid, by which the structure of the N-aryl[illegible] obtained was demonstrated, were isolated and characterized.

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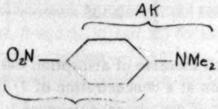
EXTRAMOLECULAR INTERACTIONS AND CHROMATICITY

V. INVESTIGATION OF THE ABSORPTION SPECTRA OF MOLECULAR COMPLEXES OF NITRO COMPOUNDS WITH AROMATIC AMINES[*]

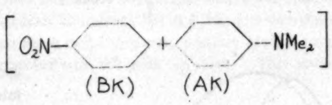
V. A. Izmailsky and A. N. Guseva

The present investigation arose in connection with a study which we carried out for compounds with "separate" non-conjugated chromophoric systems, constructed according to the A – K – Q – K – A or A – K – Q – B – K type, where K is a conjugated system; B is the electrophilic chromophore, for example, NO_2; A is the electron donor chromophore, for example, NMe_2 (Me = CH_3); and Q is the group interrupting the conjugation [1, 4, 5, 6]. We concluded that the color of such compounds arises as a consequence of the interaction of AK (donor-enoid) and BK systems (for example, nitro-enoid) with an external field through exomolecular forces,[**] similar to those which lead to formation of colored molecular complexes of the [BK + AK] type. Hence, arose the problem of investigating the absorption spectra of molecular complexes from similarly constructed chromophoric BK and AK components, and of comparing their spectra with those of compounds with separate chromophoric systems mentioned above, and also with conjugated compounds of the B – K – A type in which the same B and A groups are combined through the conjugated system K which had the same π-electron structure as in the corresponding molecular complexes.[***] A comparative study of the absorption spectra of the molecular compounds and those of the corresponding compounds with conjugated systems can lead to extremely important results for the theory of chromaticity of organic compounds.

We began our investigations with the simpler compounds, in which K was the benzene nucleus, and expressly, we set ourselves the problem of determining the position of the maximum for the molecular complex from dimethylaniline and nitrobenzene (II), and of comparing it with the position of the maximum in p-nitrodimethylaniline (I):



(I)



(II)

We stopped first at compounds with the A = NMe_2 group, expecting a stronger capacity for complex formation and a larger bathochromic effect as a consequence of the fact that this group possesses stronger electron donor properties than do many other groups, for example, NH_2, OCH_3. On the whole, the mixed chromophoric component AK = $C_6H_5NMe_2$ should possess a greater electrophobicity than the aniline molecule with the NH_2 group.

A study of the spectra of molecular complexes of compounds containing electrophilic nitro groups, with phenols, and particularly with phenolates, was of special theoretical interest.

Molecular complexes of mononitrobenzene (BK) with dimethylaniline (AK) were found to be extremely unstable (see Experimental) in solution; this agrees with the observation that we were also unable to isolate them in the solid state [7, 8, 9]. We measured the absorption spectra in pyridine at a concentration equal to 10^{-3}M for nitrobenzene ($\lambda_{max.}$ 309 mμ, $E_{max.}$ 0.67) for $C_6H_5NMe_2$ ($\lambda_{max.}$ 314 mμ, $E_{max.}$ 1.40), and calculated the absorption curve for the sum [$C_6H_5NO_2 + C_6H_5NMe_2$] in pyridine: $\lambda_{max.}$ 314 mμ, $E_{max.}$ 1.90. The spectrum of the joint solution of the complex-forming compounds 1AK : 1BK at a concentration equal to 10^{-3}M (Solution No. 4), and the values of $\lambda_{max.}$ and $E_{max.}$ were found to lie extremely close to the calculated sum of the absorption of the components forming the complex (Table 1). Under these conditions, this indicated practically complete dissociation of the complex. The displacement of $\lambda_{max.}$ was entirely negligible: $\Delta\lambda_{max.}$ + 4 mμ ($\lambda_{max.}$ 318 mμ, $E_{max.}$ 2.3). At a concentration equal to 10^{-4}M, $\lambda_{max.}$ was 311 mμ.

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[*] See previous reports [1-3].

[**] See p. 110 [1] for the basis of the term [1].

[***] See [1] for the symbols and classifications of the chromophoric groups and complex chromophoric systems.

TABLE 1

Absorption Coefficients E = log I_0/I of an Equimolar Solution of [$C_6H_5NO_2$ + $C_6H_5NMe_2$] in Pyridine at Concentrations of 10^{-3} and 10^{-4}M

λ, mμ	$C_6H_5NMe_2$	$C_6H_5NO_2$	Calculated for sum [$C_6H_5NMe_2$ + $C_6H_5NO_2$]	Solution No. 4 c = 10^{-3}M	Solution No. 5 c = 10^{-4}M
307	0.80	0.62	1.42	–	–
308	0.92	0.655	1.575	–	–
310	1.13	0.66	1.79	1.52	0.60
311	1.21	0.635	1.845	1.60	0.61
312	1.27	0.61	1.88	1.65	0.61
314	1.37	0.53	1.90	1.70	0.59
315	1.40	0.495	1.895	1.75	0.59
316	1.38	0.46	1.84	2.00	0.58
317	1.38	0.43	1.81	2.20	0.55
318	1.35	0.40	1.75	2.30	0.54
320	1.25	0.35	1.60	1.8	0.49
325	0.695	0.274	0.97	1.38	0.35
330	0.23	0.24	0.46	0.92	0.25
335	0.042	0.215	0.26	0.65	0.21
340	– 0.005	0.197	0.19	–	–
345	–	–	–	0.51	0.20
350	–	0.152	0.15	0.445	0.185
360	–	0.117	0.12	0.33	0.15
370	–	0.072	0.07	0.22	0.11
380	–	0.039	0.04	0.135	0.07

Only a small increase of absorption was found in the 400-430 mμ region at a concentration of $2 \cdot 10^{-2}$, with 3-fold excess of one of the components (experiments with Solutions No. 6 and 7 in pyridine), and with the use of the differential method of spectroscopy (see further). Thus, the nitrobenzene and dimethylaniline complex was extremely unstable and was almost completely dissociated even under conditions otherwise favorable for the formation of a complex.

We were able to determine the position of $\lambda_{max.}$, only by using nitrobenzene in an extremely large excess, namely, as a solvent. In this case it can be assumed that the equilibrium AK + BK $\rightleftharpoons$ [AK⌒BK] is strongly shifted toward formation of the complex. For [$C_6H_5NO_2$ + + $C_6H_5NMe_2$] $\lambda_{max.}$ was 429 mμ (Fig. 1, Curves 1, 2, and 3). The low values of E indicated that even in nitrobenzene the complex is highly dissociated at concentrations of 10^{-3} and 10^{-4}M (solutions No. 8 and 9, Table 2).

We have postulated [1, 15] that the interaction through exomolecular forces between molecules in the complexes may bring about the formation of a special type of partial electronic bond with the participation of π-electrons. Such a bond differs from the ordinary π-bond by the

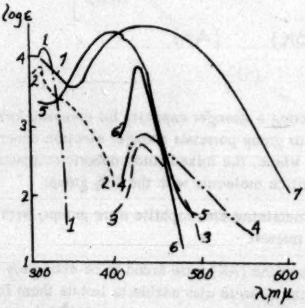


Fig. 1. Formation of molecular complexes from dimethylaniline, p-dimethylanisidine and p-nitrodimethylaniline with nitrobenzene (concentration 10^{-4}M).

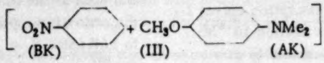
1) $C_6H_5NMe_2$ in pyridine; 2) $C_6H_5NO_2$ in pyridine; 3) [$O_2NC_6H_5$ + C_6H_5 + NMe_2] in nitrobenzene; 4) [$O_2NC_6H_5$ + $CH_3OC_6H_4NMe_2$-p] in nitrobenzene; 5) p-$O_2NC_6H_4NMe_2$ in pyridine; 6) [$O_2NC_6H_5$ + + p-$O_2NC_6H_4NMe_2$] in nitrobenzene; 7) p-$O_2NC_6H_4CH$= =$CHC_6H_4NMe_2$-p' in pyridine.

absence of an associated σ-bond; therefore, we consider it expedient to propose for it the special name of exo-bond and a special designation by the conjugation symbol (⁀) (better not dotted) with the symbol of the partial bond (AK⁀BK).

The formation of an exo-bond as a result of the linear association of two molecules is theoretically possible. In this instance the exo-bond would probably arise between the π-electrons, along a line perpendicular to the axis of the π-electrons (exo-π-bond). However, there are reasons for assuming that the bond in the complexes considered and in other types (intermediate reaction complexes) is usually brought about through an exo-p-bond as a result of a stratified association between the flat molecules lying in parallel planes. This bond arises between the π-electrons of two parallelly (or almost parallelly) situated molecules, and acts along a line connecting the axes of their π-electron clouds.

The capacity of the nitro compound (BK) for interaction and complex formation is probably increased by an increase of the electrophilicity of the compound through the introduction of additional nitro groups. Therefore, a study of the spectra of complexes with dinitrobenzene and with 2,4-dinitrostilbene is of great interest. Considering our previous observations on the greater force of the chromophoric action of the contra-polarized systems with para-positions of two electrophilic or electrophobic groups [4, 10, 11], it can be expected that the spectra of molecular complexes of the aromatic amines with p-dinitrobenzene will be shifted bathochromically, compared with the m-dinitrobenzene complexes in which there is a syn-polarizing system.

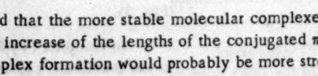
On the other hand, the capacity for interaction and complex formation of the donor-enoid AK system probably is increased through an increase of the total electrophobicity of the compound. We undertook a study of the effect on the $\lambda_{max.}$ position of an increase of the total electrophobicity of the AK system through introduction of a second donor group, for example OCH_3 (III) or $NHCOCH_3$ (Solutions of N,N-dimethyl-p-anisidine No. 11 and 12). In the present case, the introduction of OCH_3 had only a negligible effect on $\lambda_{max.}$ (+ 2 mμ), but judging from the E value (Table 2, Solutions No. 8 and 11, 9 and 12) the complex was actually somewhat more stable. But it was of greatest interest that the absorption region for the complexes (II) and (III) was displaced on the absorption region of the compound with a conjugated system (I) (Fig. 1, Curves 4 and 7).



(in nitrobenzene for $c = 10^{-3}$M $\lambda_{max.}$ was 431 mμ).

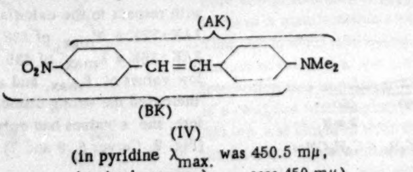
In nitrobenzene an unexpected increase of the molar absorption coefficient values was observed (Table 2, Solutions No. 8 and 9, 11 and 12) for more dilute solutions of complexes (II) and (III) at a concentration of 10^{-4}M, compared with a solution of 10^{-3}M. We assumed that these deviations were possibly a consequence of the spectrum measurement conditions, and were perhaps connected with the wide aperture. This condition showed no effect on the position of the maximum.

Further, it could be expected that the more stable molecular complexes and the phenomenon of the deeper color were perhaps obtained by an increase of the lengths of the conjugated π-electron systems. Therefore, we assumed that the capacity for complex formation would probably be more strongly expressed for the 4-nitrostilbene and the 4-dimethylaminostilbene and, proceeding from the above-indicated considerations, we understood a comparative study of the spectra of 4-nitro- dimethylaminostilbene (IV) and the corresponding molecular complex (V):



(IV)

(in pyridine $\lambda_{max.}$ was 450.5 mμ,
in nitrobenzene $\lambda_{max.}$ was 450 mμ).



(V)

(In pyridine with excess BK $\lambda_{max.}$ was 438 mμ;
with excess AK $\lambda_{max.}$ was 430 mμ.

For the [nitrostilbene + dimethylaminostilbene] complex, regardless of the presence of longer conjugated systems, the stability of the complex with a 1AK : 1BK ratio was insufficient to the same extent as a concentration of 10^{-4}M (Solution No. 18), and even at a concentration of 10^{-3}M (Solution No. 19) the spectral absorption curve was only negligibly shifted toward the longer waves, compared with the spectrum calculated for the sum of the absorption of both original compounds forming the complex. The absorption maximum of 350 mμ almost coincided with that calculated for the sum of the initial compounds (λ_{max} 355 mμ) (Fig. 2, Curves 3,4) at a concentration of 10^{-4} M, and at a concentration of 10^{-3}M the bathochromic displacement amounted to only + 30 mμ ($\lambda_{max.}$ 385 mμ). At a 1 AK : 1BK equimolar ratio of components, even at a concentration of the complex of 0.02 M, we were unable to observe the maximum expected in the region of about 430 mμ. As a consequence of the insufficient solubility of the dimethylaminostilbene in pyridine, a further increase of the concentration was impossible.

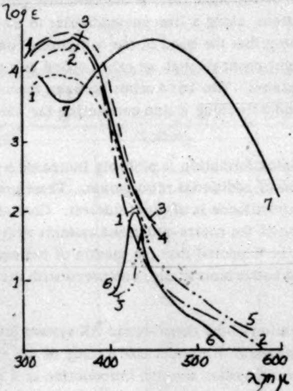


Fig. 2. [4-$O_2NC_6H_4CH=CHC_6H_5$ + $C_6H_5CH=$ (BK) $=CHC_6H_4NMe_2$-4] in pyridine. (AK)

1) BK, concentration 10^{-4}M; 2) AK, concentration 10^{-4}M; 3) sum of absorption curves 1 and 2) 4) [AK + BK], concentration 10^{-4}M; 5) [AK + BK], concentration 0.02 M at a 1AK : 3BK ratio of components (reference solution: 0.04 M BK); 6) [AK + BK], concentration 0.02 M at a 3AK : 1BK ratio of components (references solution: 0.04 M AK); 7) p-$O_2NC_6H_4CH=CHC_6H_4NMe_2$-p', concentration 10^{-4}M.

Thus, we decided to seek a method by means of which it would be possible to determine the maximum of the complex under those conditions when we could not use as the solvent one of the compounds which formed the complex. Such a method was found in the use not only of a higher concentration, but also of an excess of one of the compound, which reacted among themselves with formation of a complex (n moles per 1 mole of the complex), and in the use of the differential method for spectroscopy:[•] a solution containing (n – 1) M of the compound taken in excess, and appearing at the same time as the solvent for the complex, was used as the reference spectrum. Thus, for example, when the ratio of complex-forming compounds in the solution amounted to 1AK : 3BK (i. e., for 1 mole of the AK compound 3 moles of the BK compound was used, n = 3), a solution containing 2 moles of compound BK (3 – 1 = 2) was used as the solvent and as the reference solution.

Thus, using the indicated differential method of spectroscopy, a 3-fold excess of one of the components and a concentration of 0.02 M (experiments with Solvents No. 20 and 21), we were able to determine $\lambda_{max.}$ for complex (V) (Fig. 3).

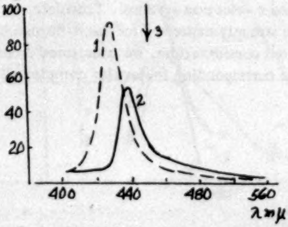


Fig. 3. [p-$O_2NC_6H_4CH=CHC_6H_5$ + $C_6H_5CH=$ (BK) $=CHC_6H_4NMe_2$-p'], concentration of [AK + BK] (AK) in pyridine 0.02 M.

Molar ratio of components: 1) 1AK : 3BK (reference solution: 0.04 M BK in pyridine); 2) 3AK : 1BK (reference solution: 0.04 M AK in pyridine); 3) p-$O_2NC_6H_4CH=CHC_6H_4NMe_2$-p' in pyridine, concentration 10^{-4}M, $\lambda_{max.}$ 450.5 mμ.

In complex (V) the absorption maximum, in relation to the maximum calculated for the sum of the components (calculated: $\lambda_{max.}$ 355 mμ, $\epsilon_{max.}$ 31,680, see Solution No. 17), was bathochromically displaced extremely strongly with respect to the calculated maximum and, namely, for 1AK : 3BK a $\lambda_{max.}$ of 438 mμ (+83), was found and for 3AK : 1BK a $\lambda_{max.}$ of 430 mμ ($\Delta\lambda$ + 75) was found. The low values of $E_{max.}$ and $\epsilon_{max.}$ (Solutions No. 20, 21) indicated the strong dissociation of the complex. Therefore, the ϵ values had only conditional ("formal") value (Fig. 2, Curves 5, 6 and 7).

If we found that under these conditions a determination of the maximum for complex [$C_6H_5NO_2$ + $C_6H_5NMe_2$] was impossible as a result of the strong dissociation, then we

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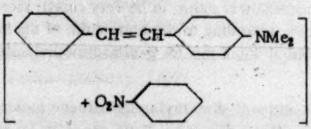
[•] As the experiments of A. V. Belotsvetov showed, this method does not apply when one of the compounds forming the complex has a strong absorption in the visible region of the spectrum, for example for dimethylaminoazobenzene.

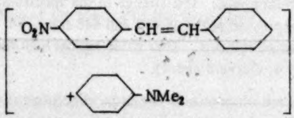
could conclude that an elongation the the conjugated π-electron systems in the components actually increases their capacity for formation of a complex. Moreover, the observed bathochromic displacement of $\lambda_{max.}$ was similar to that which we observed in the interaction of similarly constructed chromophores in conjugated systems as a result of the elongation of the K-system (cf. [3]).

Thus, we found that through exomolecular interaction of the compounds forming the complex we might obtain an effect of complex (V) from the stilbene components, very close to the effect in a conjugated system (IV).

The conjugated systems were increased in both the AK and BK components in complex (V). In order to obtain comparable data on the influence of the lengths of the conjugated chain, we undertook a study of the same spectra of the molecular complexes, with an increase of the lengths of the conjugated system only in one of the components AK or BK, and the scope of the investigation included the system [dimethylaminostilbene + nitrobenzene] (VI), and, on the other hand, [nitrostilbene + dimethylaniline] (VII).



(VI)



(VII)

(in nitrobenzene $\lambda_{max.}$ was 428 mμ, in dimethylaniline $\lambda_{max.}$ was 358 mμ).

For complex (VI) a $\lambda_{max.}$ of 428 mμ, i. e., an actual reduction of the bathochromic effect, compared with the complex (V), was found. However, here also the absorption region was shifted toward the spectrum region of compound (IV) (Fig. 4, Curves 1 and 2).

In a study of the absorption spectra of molecular complexes with p-dimethylaminostilbene, we encountered its insufficient solubility in alcohol. Because of this we decided to use pyridine as the solvent.

It is necessary to note here that generally the solvent had an extremely great effect on the stability of the complexes and on their color. During the investigation of the molecular complexes of quinoline and pyridine salts with the aromatic amines [2,3], we encountered an influence of the solvent on the spectrum and on the stability of the complex.

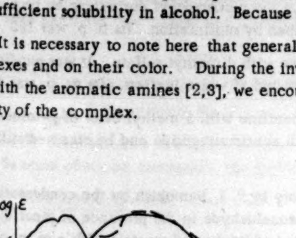


Fig. 4. Solutions of 4-dimethylaminostilbene and 4,4'-nitrodimethylaminostilbene in pyridine and nitrobenzene.
1) 4-Dimethylaminostilbene in pyridine, concentration 10^{-4}M; 2) the same in nitrobenzene, concentration 10^{-4}M; 3) 4,4'-nitrodimethylaminostilbene in pyridine, concentration 10^{-5}M; 4) the same in nitrobenzene, concentration 10^{-5}M.

The molecular complexes were more stable in pyridine than in ethanol. In benzene and in ether a complete disappearance of the optical effect of the interaction of the compounds which formed the complex was often observed in benzene and in ether.

In complex (V), with an excess of dimethylaminostilbene (AK), we observed a hypsochromic effect ($\lambda_{max.}$ 430 mμ), compared with the solution containing an excess of nitro component (BK) ($\lambda_{max.}$ 438 mμ). Apparently, here we have a manifestation of a frequently observed rule. Thus, for systems containing a large excess of dimethylaniline in relation to the nitro compounds, the effect of the interaction in a number of cases disappeared; no formation of a complex with an absorption in the region of about 430 mμ was observed with the use of dimethylaniline as the solvent. Whereas for p-dimethylaminostilbene in nitrobenzene (VI), $\lambda_{max.}$ was 428 mμ, for a solution of p-nitrostilbene in dimethylaniline (VII) we observed only a $\lambda_{max.}$ 358 mμ, i. e., the effect was almost absent.

It was of further interest to explain whether the interaction of nitrobenzene, with a bathochromic effect, on a molecule in which the dimethylamino group was conjugated with a nitro group system, was possible. In the p-nitrodimethylaniline molecule we actually observed this capacity: a strong bathochromic displacement of the maximum $\lambda_{\text{max.}}$ 429 mμ, instead of 390-395 mμ, indicated the formation of the complex [p-$O_2NC_6H_4NMe_2 + C_6H_5NO_2$] (Fig. 1, Curves 5 and 6).

The capacity of p-nitrodimethylaniline for intermolecular interaction with the nitrobenzene which we established agrees with Gibson and Loeffler's observation for p-nitroaniline [16]. However, these authors did not study the absorption spectra, and their conclusion was made on the basis of an investigation of the transmission of light by an equimolar mixture of p-nitroaniline and nitrobenzene. The conclusion of the intermolecular effects was made on the basis of the observation that a bend of the curve at about 465 mμ changed its position under the influence of pressure. Moreover, the authors noted that in the longer wave regions (500-600 mμ) absorption was found to be insensitive to pressure and therefore, should probably be attributed to the p-nitroaniline itself. However, it should be considered that the absorption of p-nitroaniline itself disappears in the longer wave regions.about 470 mμ [17].

Unlike p-nitromethylaniline, the p-nitrodimethylaminostilbene molecule was found to be extremely stable with respect to nitrobenzene. The change of the spectrum in nitrobenzene was shown to be very small; there were two indistinctly expressed peaks at 452 and 448 mμ.* On the average, according to the half-width of the band, the maximum lies at 450 mμ. This value agrees with the maximum of 450.5 mμ for p-nitrodimethylaminostilbene in pyridine (Fig. 4, Curve 3 and 4).

From these observations it can be concluded that in the 4-nitro-4'-dimethylaminostilbene molecule the system is so much closed in itself (as a result of mutual intramolecular effects) that it has little capacity for extramolecular interactions. If this conclusion is correct, then a sharp difference in the effects of polar and non-polar solvents on the absorption spectra (on the position of the maximum and the molar absorption coefficient) should be absent.

EXPERIMENTAL

A. Synthesis and Purity Ratings of the Preparations

Nitrobenzene was purified by freezing and by distillation. Its b. p. was 209°.

Dimethylaniline – the commercial preparation – was freed from the monomethyl derivative by treatment with acetic anhydride, by steam-distillation of the dimethylaniline, and then by sublimation. Its b. p. was 193°.

p-Dimethylanisidine was obtained by methylation of p-anisidine with dimethyl sulfate. It was purified by steam-distillation and by recrystallization from 50% alcohol. It consisted of white leaflets. Its m. p. was 48°.

p-Nitrodimethylaniline was obtained by methylation of p-nitroaniline with a methyl ester of p-toluenesulfo acid. It was freed from the monomethyl derivative by treatment with acetic anhydride and by steam-distillation. Its m. p. was 162°.

4-Nitro-4'-dimethylaminostilbene was obtained in our laboratory by P. I. Samokish by the condensation of 4-nitrophenylacetic acid (m. p. 150.5-152°) with 4-dimethylaminobenzaldehyde in the presence of piperidine. After recrystallization from alcohol and then from pyridine it consisted of bright-red crystals with a m. p. of 149.5-150° [12].

4-Nitrostilbene was obtained by P. I. Samokish by the condensation of 4-nitrophenylacetic acid with benzaldehyde in the presence of piperidine. From ethyl alcohol the needles were of a light-yellow color with a m. p. of 154-155° [13].

For the first time, 4-dimethylaminostilbene was obtained from anhydrous alcohol, as colorless leaflets with a m. p. of 147-148° by the distillation of 4-dimethylaminophenylbenzylcarbinol under reduced pressure [14].

We selected a new method, namely, the condensation of phenylacetic acid and p-dimethylaminobenzaldehyde in the presence of piperidine. 10 g of p-dimethylaminobenzaldehyde, carefully mixed with 10 g of pure phenylacetic acid and 5 ml of piperidine, was heated for 4 hours at an internal temperature of 140-150° in a three-necked flask equipped with a thermometer and a mechanical stirrer. On completion of the heating, the mixture was treated with boiling water (several portions). The residue was recrystallized from pyridine.

From pyridine and from anhydrous alcohol it consisted of light-weight, colorless leaflets with a m. p. of 147.5-148°, which agreed with the literature values [14].

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* On a logarithmic curve these peaks disappeared.

On long storage the crystal surfaces became brownish, therefore, we had to use only the freshly-recrystallized preparation for the spectroscopic measurements.

B. Investigation of the Absorption Spectra

The spectroscopic measurements were carried out with a Beckmann photoelectric photometer at a layer depth of 1 cm for the most part, which offered no possibility of carrying out spectrum measurements at higher concentrations. Later we used quartz inserts (Schultz plates) in a cuvette of 1.0 cm in order to obtain layers with a depth of 0.10 and 0.01 cm.

The measurements were carried out through every 5 mμ, but through every 1-2 mμ in the positions of maxima and bends.

The molar absorption coefficient ε was probably not accurately determined, as a consequence of the fact that the complex was dissociated to a greater or lesser extent and its concentration was unknown. The calculated values of ε can be used only conditionally for comparison of the degrees of complex formation. Essentially, we had to consider the absorption coefficients $E = \log I_0/I$, in investigation of the spectra of the complexes.

The essence of the differential method which we used for the investigation of the spectra of the complex compounds is stated above (p. 1407).

1. Investigation of Solutions of [Nitrobenzene + Dimethylaniline] (Complex II)

Symbols: AK = $C_6H_5NMe_2$; BK = $C_6H_5NO_2$.

a) Solutions in ethanol.

No. 1. The solution of equimolar quantities of the components (1AK : 1BK), at a concentration equal to 0.02 M for each compound, was not colored. No maximum was observed in the 400-430 mμ region. There was dissociation of the complex.

No. 2. At a concentration of 0.1 M for each component, 1AK : 1BK, a yellow color appeared; however, the formation of a complex became insignificant in this case also, so that a maximum was absent in the 400-430 mμ region. For example, the following E values in the presence of some interaction were found:

λ mμ	400	410	420	430	440
E for solution No. 1	0.414	0.179	0.067	0.024	0.013
E for solution No. 2	1.32	0.705	0.420	0.302	0.234

No. 3. The solution had an AK concentration equal to 0.2 M and a BK concentration equal to 0.02 M. (10AK : 1BK). Because of strong absorption, the spectrum could not be measured with a cuvette of 1 cm.

b) Solutions in pyridine. They were considerably more deeply colored than in alcohol at the same concentrations.

No. 4. With an equimolar ratio (1AK : 1BK) and concentration for each component equal to 10^{-3}M, a $\lambda_{max.}$ of 318 mμ and an $E_{max.}$ of 2.3 was found (Table 1).

No. 5. For each of the components a $\lambda_{max.}$ of 311 mμ, and a $E_{max.}$ of 0.61 (Table 1) was found at an equimolar ratio of 1AK : 1BK and a concentration equal to 10^{-4}M.

No. 6. At a 3AK : 1BK ratio and an AK concentration equal to 0.6 M, and a BK concentration of 0.02 M (reference solution: 0.04 M AK in pyridine), no maximum was observed in the region of about 330 mμ.

No. 7. With a 1AK : 3BK ratio and an AK concentration of 0.02 M, and a BK concentration of 0.06 M (reference solution: 0.04 M BK in pyridine), no maximum was observed in the region of about 330 mμ.

c) Solutions in nitrobenzene. The ratio was 1AK : ∞ BK.

No. 8. For a solution of $C_6H_5NMe_2$ in nitrobenzene, at a concentration of $1 \cdot 10^{-3}$ M $\lambda_{max.}$ was 429 mμ, and $E_{max.}$ was 0.20 (Table 1).

The color of the solution was yellow-orange.

No. 9. For a solution of $C_6H_5NMe_2$ at a concentration equal to $0.95 \cdot 10^{-4}$ M, $\lambda_{max.}$ was 428.5 mμ, and $E_{max.}$ was 0.048 (Table 1 and Fig. 1, Curve 3).

No. 10. The solution of $C_6H_5NMe_2$ had a concentration of $3.1 \cdot 10^{-2}$M. No measurements of the maximum were given at d = 1.0 cm.

2. Investigation of Solutions of p-$CH_3OC_6H_4NMe_2$ in Nitrobenzene (Complex III)

The ratio was 1AK : ∞BK; BK = $C_6H_5NO_2$ and AK = N,N-dimethyl-p-anisidine.

No. 11. At a concentration of $1.04 \cdot 10^{-3}$M: $\lambda_{max.}$ 431 mμ, $E_{max.}$ was 0.402 mμ (Table 2).

No. 12. At a concentration of $0.84 \cdot 10^{-4}$M: $\lambda_{max.}$ was 428.5 mμ, and $E_{max.}$ was 0.060.

However, if one considers that at 428 and 429 mμ only an extremely insignificant cusp is observed, compared with an E of 0.059 at 430, 431 and 432 mμ, then it will be more correct to assume for $\lambda_{max.}$ the value 430 mμ, found by calculation from the half-width of the band of the region from 427 to 433 mμ (Table 2, Fig. 1, Curve 4).

No. 13. We were unable to measure the maximum at a concentration of $6.8 \cdot 10^{-2}$ M and d = 1.0 cm.

3. Investigation of a Solution of p-Dimethylaminostilbene in Nitrobenzene (Complex VI)

The ratio was 1AK : ∞BK.

No. 14. 4-$Me_2NC_6H_4CH{=}CHC_6H_5$ (AK) was dissolved in nitrobenzene (BK).

The concentration was $0.83 \cdot 10^{-4}$M; $\lambda_{max.}$ 430 mμ, $E_{max.}$ 0.207 (Table 2, Fig. 4, Curve 2).

TABLE 2

Absorption Coefficients $E = \log I_0/I$

λ mμ	Solution Nos.				
	8, c = 10^{-3}	9, c = $0.95 \cdot 10^{-4}$	11, c = $1.04 \cdot 10^{-3}$	12, c = $0.84 \cdot 10^{-4}$	14, c = $0.83 \cdot 10^{-4}$
400	0.030	0.006	0.096	0.014	0.040
405	–	–	0.098	0.014	0.042
410	0.033	0.007	0.100	0.015	0.043
415	–	0.010	0.143	0.026	0.045
420	0.109	0.025	0.163	0.035	0.062
422	0.140	0.033	–	0.044	–
424	0.171	0.039	–	0.050	–
425	–	–	0.292	–	0.165
426	0.194	0.045	0.312	0.057	–
427	0.199	0.047	0.324	0.058	–
428	0.199	0.048	0.334	0.060	0.205
429	0.200	0.048	0.338	0.060	–
430	0.197	0.047	0.340	0.059	0.207
431	0.192	0.047	0.402	0.059	–
432	0.188	0.045	0.338	0.059	0.202
433	0.182	0.044	0.335	0.058	–
434	0.177	–	0.333	–	0.195
435	0.170	0.042	0.329	0.056	–
436	0.166	–	–	–	0.185
438	0.157	–	–	–	0.178
440	0.149	0.037	0.310	0.051	0.170
445	0.131	0.031	0.288	0.043	–
450	0.112	0.027	0.268	0.039	0.135
455	0.098	0.023	0.247	0.037	–
460	0.082	0.020	0.230	0.035	0.103
470	0.058	0.014	–	0.026	–
480	0.037	0.009	0.157	0.022	0.060
490	0.025	0.005	–	0.016	–
500	0.014	0.002	0.100	0.012	0.033
520	–	–	0.062	0.007	0.020
540	–	–	0.020	0.003	0.012

The yellow color of the solution was appreciably deeper than that of the nitrobenzene itself or of a solution of dimethylaminostilbene in alcohol.

4. Investigation of Solutions with 4-Dimethylaminostilbene and 4-Nitrostilbene (Complex V) in Pyridine

Symbols: AK = $C_6H_5CH{=}CHC_6H_4NMe_2$-p; BK = $C_6H_5CH{=}CHC_6H_4NO_2$-p.

No. 15. The BK in pyridine was at a concentration of 10^{-4} M; $\lambda_{max.}$ was 342.5 mμ, as the average of the four values of 341-344 mμ, with the same E of 0.905, and $\epsilon_{max.}$ of 23,000; log $\epsilon_{max.}$ was 4.36 (Fig. 2, Curve 1);

No. 16. The AK in pyridine was at a concentration of 10^{-4} M: $\lambda_{max.}$ was 356 mμ for an $E_{max.}$ of 2.30; $\epsilon_{max.}$ was 9050; log $\epsilon_{max.}$ was 3.96 (Fig. 2, Curve 2).

No. 17. The calculated sum of absorption for [AK + BK] in pyridine was on the basis of No. 15 and 16; and a concentration of 10^{-4} M (Fig. 2): $\lambda_{max.}$ was 355 mμ for $E_{max.}$ of 3.19; $\epsilon_{max.}$ 31,860; log $\epsilon_{max.}$ was 4.50 (Fig. 2, Curve 3).

No. 18. The solution of 1AK : 1BK in pyridine was at a concentration of 10^{-4}M for each compound forming the complex.

The position of the maximum could not be accurately measured for d = 1.0 cm, as a consequence of the strong absorption. The approximate position of the maximum could be calculated from the half-width of the band between 320 and 380 mμ for the same E of 2.7. We found then, that $\lambda_{max.}$ lay at about 350 mμ, which almost coincided with the value calculated for the sum of the compounds taken (cf. Solution No. 17; Fig. 2, Curve 4).

If the determined values of E are compared with the calculated values, then it can be concluded that some interaction is observed between the AK and BK component at a concentration of 10^{-4} M and at a ratio of 1AK : 1BK. The present AK component was thus found to be more active than $C_6H_5NMe_2$.

No. 19. The solution in pyridine (1AK : 1BK) was at a concentration equal to 10^{-3}M for each component. A $\lambda_{max.}$ of 385 mμ at $E_{max.}$ of 2.00 was found; ε 2000; log $\epsilon_{max.}$ was 3.35.

According to the position of the maximum, it can be concluded that the main bulk of the mixture does not enter into complex formation (cf. No. 5 and No. 16). However, by calculation for the sum of the components (No. 17) a bathochromic displacement of $\Delta\lambda_{max.}$ = + 30 mμ, compared with a $\lambda_{max.}$ of 355 mμ, indicated that at concentration equal to 10^{-3} M, and at a molar ratio of the components, complex formation was already considerably greater than at a concentration of 10^{-4} M.

No. 20, and 21. The solutions of p-nitrostilbene and p-dimethylaminostilbene were with a 3-fold excess of one of the components (Fig. 3 and Fig. 2, Curves 5 and 6).

Solution No.	Ratio of components in solution, in moles	$\lambda_{max.}$ in mμ	$E_{max.}$	Concentration in pyridine (M)		Reference solvent in pyridine (M)
				AK	BK	
20	1AK* : 3BK**	438	1.09	0.02	0.06	BK 0.04
21	3AK : 1BK	430	1.86	0.06	0.02	AK 0.04

5. Investigation of Solutions of $p\text{-}O_2NC_6H_4NMe_2 + C_6H_5NO_2$ in Pyridine and in Nitrobenzene

No. 22. The p-nitrodimethylamiline in pyridine was at a concentration of 10^{-4}M: $\lambda_{max.}$ 396 mμ at an $E_{max.}$ of 2.00; $\epsilon_{max.}$ was 20,000; log $\epsilon_{max.}$ was 4.30 (see Fig. 1, Curve 5).

No. 23. The p-nitrodimethylaniline in nitrobenzene was at a concentration equal to 10^{-4} M. For the complex $[p\text{-}O_2NC_6H_4NMe_2 + C_6H_5NO_2]$ $\lambda_{max.}$ was 420 mμ at an $E_{max.}$ of 0.720, $\epsilon_{max.}$ was 7200, log $\epsilon_{max.}$ was 3.86 (Fig. 1, cf. Curve 6 and Curve 7).

No maximum could be observed for a concentration of 10^{-3} M.

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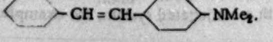
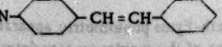
* AK: 

** BK: 

6. Investigation of Solutions of 4-$O_2NC_6H_4CH$= $CHC_6H_4NMe_2$-4' in Pyridine and in Nitrobenzene

No. 24. The solution in pyridine was at a concentration of 10^{-5} M $\lambda_{max.}$ was 451 mμ; $\epsilon_{max.}$ was 26,900, and log $\epsilon_{max.}$ was 4.43 (Fig. 4, Curve 3).

No. 25. The solution in pyridine at a concentration of 10^{-4} M had a $\lambda_{max.}$ of 450 mμ, and a log $\epsilon_{max.}$ of 4.41.

We obtained the following as the average of the measurements with Solutions No. 24 and 25 with the Beckmann photoelectric spectrophotometer: a $\lambda_{max.}$ of 450.5 mμ, and a log $\epsilon_{max.}$ of 4.42. These figures agree well with P. I. Samokish's data, obtained with a spectrograph by the photographic method: a $\lambda_{max.}$ of 450.5 mμ, and a log $\epsilon_{max.}$ of 4.45 [1]•.

No. 26. No maximum could be accurately measured for a solution in pyridine at a concentration equal to 10^{-2} M. We obtained a $\lambda_{max.}$ of about 455 mμ if we take the average between 450 and 460 mμ at a log $\epsilon_{max.}$ of 3.91. Moreover, the upper part of the curve in the region of the maximum is shifted rather considerably toward the smaller log ϵ values, compared with No. 24 and 25. It is possible that this is a consequence of intermolecular interaction of nitrodimethylaminostilbene itself at higher concentrations. It is necessary to verify these observations because of their importance.

No. 27. The solution in nitrobenzene was at a concentration equal to $0.83 \cdot 10^{-4}$ M.

Two closely-lying maximum of α $\lambda_{max.}$ of 452.5 mμ and β $\lambda_{max.}$ of 448 mμ (at $E > 2$) were observed. Between the maxima at 449, 450, and 451 mμ there was only an extremely small decrease of E to 2.00.

No. 28. The solution in nitrobenzene was at a concentration equal to $0.83 \cdot 10^{-5}$ M.

Just as for No. 27, two closely-lying maxima were observed: α $\lambda_{max.}$ at 452 mμ ($E_{max.}$ was 0.218, $\epsilon_{max.}$ was 26,170, log $\epsilon_{max.}$ was 4.41), and β $\lambda_{max.}$ was 448 mμ ($E_{max.}$ was 0.218, $\epsilon_{max.}$ was 26,170, log $\epsilon_{max.}$ 4.41).

Between the maxima there was only an extremely small decrease of E to 0.217 (E 26,060, log ϵ 4.416) (Fig. 4, Curve 4).

If the position of the maximum band is determined by the average from the half-width, then it can be assumed that $\lambda_{max.}$ for solutions in nitrobenzene lies at about 450 mμ at concentrations of 10^{-4}-10^{-5} M. No bathochromic displacement of the maximum was observed, compared with the position of the maximum in a solution of pyridine, as it was for p-nitrodimethylaniline (No. 23). In the present case nitrobenzene showed no reaction, and no formation of a complex with nitrobenzene occurred.

SUMMARY

1. The absorption spectrum of a solution of [$C_6H_5NO_2 + C_6H_5NMe_2$] in pyridine at concentrations of 10^{-3} and 10^{-4} M almost coincided with the spectrum calculated for the sum of the components, which indicates the almost complete absence of formation of a complex.

The equilibrium $AK + BK \rightleftharpoons [AK \frown BK]$ may be shifted toward the complex, using nitrobenzene as the solvent; $\lambda_{max.}$ was 429 mμ.

2. The absorption spectra of 4-nitrostilbene, dimethylaminostilbene and 4-nitro-4'-dimethylaminostilbene in pyridine were measured.

Using a 3-fold excess of one of the components, an increased concentration of 0.02 M, and the differential method for spectroscopy, wer were able to determine the position of the maximum for the complex [$O_2NC_6H_4CH$= =$CHC_6H_5 + C_6H_5CH$= $CHC_6H_4NMe_2$] in pyridine; $\lambda_{max.}$ was 438 mμ with an excess of the nitro compound and 430 mμ for an excess of the amino compound.

3. For solutions of p-dimethylaminoanisole and p-dimethylaminostilbene in nitrobenzene the position of the maximum was found to be in the region close to 430 mμ.

4. The observation was made that, with an excess of the nitro component (BK), $\lambda_{max.}$ for the complex can lie in the longer wave region than for the corresponding compound with a conjugated system, for example, for the

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• It was a Hilger (13 X 18 "Intermediate" Model) spectrograph with a Sheib-Fyuss photometric apparatus with a rotating sector. The intensity of blackening on the spectrogram in the area of the maximum was determined by means of a Zeiss microphotometer.

complex (II) compared with (I), and (V) compared with (VI).

With an excess of the dimethyl amino component (AK) in solution, a shift of the maximum toward the shorter waves was observed, and in some cases the effect of interaction with the formation of a colored complex was absent. Thus, for a solution of 4-nitrostilbene in dimethylaniline $\lambda_{max.}$ was 358 mμ.

5. A $\lambda_{max.}$ of 429 mμ ($\lambda_{max.}$ in pyridine was 395 mμ) was found for a solution of p-nitrodimethylaniline in nitrobenzene. No change was observed for the position of the maximum for p,p'-nitrodimethylaminostilbene in nitrobenzene (450 mμ), compared with a solution in pyridine.

6. In certain cases the region of absorption of a molecular complex of the (AK + BK) type can lie extremely close (and sometimes even in the longer wave region) to the region of absorption for a compound with a conjugated system of the $A-\overset{}{K}-B$ type, which contains the same AK and BK polar systems in the molecule.

The reduction of the energy of excitation as a result of the interaction through exo-forces of two polar-antithetical chromophoric systems in the complex is perhaps extremely close to the effect observed for interaction of the same chromophoric systems through endo-forces in a molecule with a conjugated system.

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INVESTIGATION OF COMPLEX COMPOUNDS OF $Met[BAr_4]$

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In previous works we reported on the results of an investigation of borate-onic compounds. On shaking chloroform solutions of $Met[B(C_6H_5)_4]$[1] or $Met[BAr_3Ar']$[2] with mercury at ordinary temperature, a free-radical transition reaction of one of the anion radicals to mercury occurs, with the formation of diarylmercury. It was shown that for an anion having two different radicals, the breaking away of naphthyl- and p-tolyl radicals chiefly, compared to phenyl, proceeds. The same sequence of breaking away was observed on thermal decomposition of $NH_4[BAr_3Ar']$, i.e., a splitting off of the more electronegative radical took place.

In the present work we attempted to extend the investigation of those types of compounds which will also have aliphatic radicals in the $[BR_4]$ anion, and to study the reactions of the anions, which take place with the breaking away of one radical. Derivatives with alkyl radicals in the anion have been investigated very little as yet. A series of dialkyl and arylalkyl mixed derivatives, which were substituted in the anion, have been described: $Li[B(CH_3)_3C_2H_5]$[3], $Li[BC_6H_5(C_4H_9)_3]$[4], $Li[B(C_6H_5)_3C_4H_9]$[5], and $Li[B(C_6H_5)_3C \equiv CC_6H_5]$[6], but they are unstable, and all of them except the last are obtained only in solutions.

We attempted to obtain from $(C_6H_5)_3B$ and CH_3Li or from $(\alpha\text{-}C_{10}H_7)_3B$ and C_2H_5Li the corresponding complex compounds $Li[B(CH_3)(C_6H_5)_3]$ or $Li[BC_2H_5(C_{10}H_7)_3]$. The precipitates obtained by mixing solutions of the indicated components were not very stable, and quickly decomposed on storage in the air. The aqueous solutions of the compounds just obtained gave no precipitates with potassium or ammonium salts. However, on standing of the above-indicated solutions, an increasingly complete separation of precipitates with K and NH_4 cations was initiated. An analysis of the precipitates showed that they consisted of $K[B(C_6H_5)_4]$ and $K[B(C_{10}H_7)_4]$ or the corresponding ammonium derivatives. Thus, it can be assumed that in the solutions, a symmetrization of the $[B(CH_3)(C_6H_5)_3]^-$ and $[B(C_2H_5)(C_{10}H_7)_3]^-$ anions occurs. In this reaction, there is an analogy with the symmetrization of the asymmetrical compounds of trivalent boron. Thus, for example, a mixture of triethylboron and triphenylboron was obtained on attempts to synthesize diethylphenylboron [7].

In work with $K[B(C_6H_5)_4]$, which was very difficultly soluble in water, an interesting peculiarity was observed: the potassium complex was soluble in acetone, the monomethyl ether of ethylene glycol, and in some other solvents. On addition of water to the solution, the solubility increased, reaching a maximum with the addition of approximately 20% water, then the solubility decreased, and with a large excess of water the complex precipitated completely from solution. On heating of solutions of $K[B(C_6H_5)_4]$ in the monoethyl ether of ethylene glycol, a quantitative breaking away of one phenyl radical results, which takes up hydrogen of the solvent, forming benzene. The solution acquires a brown color. On treatment of the solution, the usual decomposition products of triphenylboron – phenyl and diphenylboric acid – are separated by the action of air and water. The reaction probably takes place according to the equation

$$K[B(C_6H_5)_4] + C_2H_5OCH_2CH_2OH \longrightarrow C_6H_6 + (C_6H_5)_3B + C_2H_5OK + CH_3CHO$$

$$(C_6H_5)_3B \xrightarrow{(O)} (C_6H_5)_2BOC_6H_5 \xrightarrow{H_2O} (C_6H_5)_2BOH + C_6H_5OH.$$

The presence of acetaldehyde in the solution was demonstrated by precipitation of the dimedon derivative. A major portion of the aldehyde was resinified by the action of alkali. On heating of solutions of $NH_4[B(C_6H_5)_4]$ in the monoethyl ether of ethylene glycol or in methanol at 100° in a sealed tube, the splitting off of one phenyl group as benzene also results. Ammonia, triphenylboron (by its decomposition products) and triphenylboron ammoniate were found in the solution. In the present case, it is impossible to say whether an analogous reaction proceeds with the solvent as with the potassium derivative, or whether intramolecular decomposition occurs

$$NH_4[B(C_6H_5)_4] \longrightarrow C_6H_6 + NH_3 + B(C_6H_5)_3.$$

Since the breaking away of one radical proceeds for the reaction described, it would be possible to use the reaction for the determination of the stability of the bond of different radicals with boron in the $[BAr_3AR]^-$ anion. For $K[B(C_6H_5)_3Ar]$, where Ar is α-naphthyl or p-tolyl an almost quantitative breaking away of only the Ar-radical results.

A decomposition of the complexes is observed on exposure of their chloroform solutions to ultraviolet light. Solutions of $Li[B(C_6H_5)_4]$ or $K[B(C_6H_5)_4]$ are decomposed with the breaking away of the phenyl radical which, taking up the hydrogen of the solvent, gives benzene, or on dimerization, forms biphenyl. Due to the chlorine of the chloroform, the metals Li or K yield chlorides. This photoreaction of borate-onic compounds has some similarity to the photoreactions of the -onic compounds. Thus, for example, a deamination reaction proceeds on exposure of alcoholic solutions of the diazo salts and, moreover, the resulting radical breaks away the hydrogen of the solvent [8].

Another type of reaction of the breaking away of one radical from an anion proceeds by the action of bromine on the complexes. In the literature we encountered only one indication for reactions of halides with the complexes, namely, the action of iodine on $Li[B(C_6H_5)_3C\equiv CC_6H_5]$, which takes place with the breaking away of the phenylacetylene radical from the anion. We studied the reaction of $K[B(C_6H_5)_4]$ with bromine, which proceeds according to the equation

$$K[B(C_6H_5)_4] + Br_2 \longrightarrow KBr + C_6H_5Br + (C_6H_5)_3B.$$

In the bromination reaction of complex compounds with $[B(C_6H_5)_3Ar]^-$ anion, the same sequence of the breaking away of radicals is observed. Thus, the reaction proceeds smoothly:

$$Li[B(C_6H_5)_3C_6H_4CH_3] + Br_2 \longrightarrow LiBr + CH_3C_6H_4Br + (C_6H_5)_3B.$$

Together with the decomposition of the complex compounds by halides, an attempt was made to use anhydrous ferric chloride in nonaqueous solvents for this purpose. It is known that in an aqueous solution, by the action of the chlorides of metals like Fe^{++}, Co^{++}, Ni^{++}, Mn^{++}, the formation of hydroxides of the metals and benzene occurs [6]:

$$2Li[B(C_6H_5)_4] + MetCl_2 + 6H_2O \longrightarrow Met(OH)_2 + 2LiCl + 2C_6H_5B(OH)_2 + 6C_6H_6.$$

In an ether solution, the reactions of reduction of the chloride of the metal and of formation of biphenyl are observed, which are explained by the decomposition of the $[B(C_6H_5)_4]^-$ anion, losing one electron during the reduction of the metal

$$2Li[B(C_6H_5)_4] + 2CuCl_2 \longrightarrow 2CuCl + 2LiCl + 2(C_6H_5)_3B + C_6H_5C_6H_5.$$

On further reaction with an excess of the complex, cuprous chloride is reduced to the metal.

The reaction of $Li[B(C_6H_5)_4]$ with ferric chloride in an acetone solution, which we studied, proceeded peculiarly: lithium chloride, biphenyl, benzene and phenylboric acid (after treatment of the reaction mixture with water) were formed. The reaction may be represented by the following equations:

$$Li[B(C_6H_5)_4] + 3FeCl_3 \longrightarrow LiCl + C_6H_5BCl_2 + 3FeCl_2 + C_6H_5C_6H_5 + C_6H_5$$

$$C_6H_5 \xrightarrow{\text{acetone}} C_6H_6.$$

The mechanism of this reaction requires further elucidation.

From the examples cited of the decomposition of the $[BR_4]$ anion, it is evident that in the most diverse reactions the same sequence of the breaking away of the radicals from boron is maintained.

EXPERIMENTAL

Lithium triphenylmethylborate $Li[B(C_6H_5)_3CH_3]$. An ether solution of methyllithium, obtained from CH_3I and Li [9], was added slowly to an ether solution of 2.4 g (0.01 mole) of $(C_6H_5)_3B$ in nitrogen. In all, 30 ml of a 0.3 N solution of CH_3Li (~0.01 mole) was introduced. On addition of the organo-Li compound, a slight evolution of heat of the reaction mixture was observed. The solvent was removed, and the viscous substance which formed was quickly transferred to a beaker. The latter was placed in a vacuum-desiccator. Ether was removed from the substance at low vacuum. On removal of the ether the contents of the beaker were crystallized. The crystalline precipitate quickly decomposed in the air, with the formation of an oily product. An appreciable odor of ether was observed, and a small quantity of biphenyl was separated by the rapid dissolving of the precipitate in water. The aqueous filtrate had an alkaline reaction to litmus.

Fresh aqueous solutions of the resulting complex yielded no precipitate with K- and NH_4- salts. In time, an appreciable separation of the water-insoluble precipitates in both cases was observed. The ammonium derivative was filtered off, dried and analyzed for its nitrogen content. The latter corresponded to $NH_4[B(C_6H_5)_4]$.

Found %: N 4.33. $C_{24}H_{24}BN$. Calculated %: N 4.16.

Lithium trinaphthylethylborate $Li[B(C_{10}H_7)_3C_2H_5]$. A 1.15 N solution of C_2H_5Li [10] was added slowly to a solution of 5.54 g (0.01 mole) of $(C_{10}H_7)_3B \cdot 2C_6H_6$ in 50 ml of anhydrous ether in a current of nitrogen. In all, 9 ml of a benzene solution of ethyllithium (free of LiBr) was introduced. The ether in the reaction flask boiled up vigorously on addition of the ethyllithium. The mixture was allowed to stand in an atmosphere of nitrogen for several hours. Then the white precipitate which came down was filtered off, washed with benzene and dried in a vacuum-desiccator for 2 hours at 5 mm pressure. 2.5 g of the precipitate was obtained. The precipitate decomposed in the air. It dissolved well in water with a slight turbidity of the solution. An aqueous solution of the resulting compound at first gave no precipitate formation with a KCl and NH_4Cl solution. The formation of water-insoluble, white precipitates with KCl and NH_4Cl was observed after several hours of standing of the solutions. The ammonium derivative was filtered off, washed carefully with water and dried in a vacuum-desiccator. The analytical determination of nitrogen in the compound corresponded to the presence of an NH_4-complex with four naphthyl groups in its anion.

Found %: N 2.78. $C_{40}H_{32}BN$. Calculated %: N 2.61.

Reaction of $K[B(C_6H_5)_4]$ with the monoethyl ether of ethylene glycol. 5 g (0.014 mole) of potassium tetraphenylborate was dissolved in a mixture of 80 ml of the monoethyl ether of ethylene glycol and 20 ml of water. The resulting clear solution was heated for 5-7 hours in a flask with a reflux condenser. At the end of the heating, the mixture was a dark-brown color and had an alkaline reaction to litmus. After the heating, 50 ml of water and 5 ml of 2% alkali were added to the reaction flask, and the benzene which separated was steam-distilled. 1.3 ml (1.04 g) of benzene separated, which amounted to 94% of the theoretical, from the calculation for the breaking away of one phenyl radical from the anion of the complex. The benzene was nitrated with m-dinitrobenzene with a m.p. of 90°. A test of a mixture with pure m-dinitrobenzene gave no melting point depression.

After separation of the benzene, acetaldehyde was determined in the water residue as the dimedon derivative with a m.p. of 140°. A test sample of a mixture with the derivative obtained for pure acetaldehyde melted without a melting point depression.

After removal of the benzene the alkaline residue was acidified with sulfuric acid to an acid reaction to Congo, and was again steam-distilled. Phenol was observed in the water residue. By the action of bromine water, a bromination product of phenol, tribromophenol, was separated in the quantity of 2 g, with a m.p. of 93° (from alcohol), without a depression with the pure substance. Considering that 1 mole of phenol is formed by the oxidation of 1 mole of triphenylboron, the resulting yield of the former, based on the quantity of tribromophenol, amounted to 60% of the theoretical.

After steam-distillation of the phenol, an oil with the characteristic odor of diphenylboric acid, which melted in hot water, remained in the flask. The resulting oil was not investigated closely.

No potassium tetraphenylboron was observed after the reaction. Thus, the reaction went to completion.

Reaction of $NH_4[B(C_6H_5)_4]$ with the monoethyl ether of ethylene glycol. 3.36 g (0.01 mole) of the complex in 75 ml of the monoethyl ether of ethylene glycol and 25 ml of water was heated for 2 hours at boiling. No evolution of gaseous NH_3 was observed. The solvent was removed. The first 20 ml of the distillate was diluted with water. 1 ml (0.8 g) of benzene, corresponding to the breaking away of one phenyl group, was formed.

The presence of phenol in the water layer was demonstrated qualitatively by its reaction with bromine. The tribromophenol (0.4 g) which separated had a m.p. of 93°. In the flask after steam-distillation was an oil which had the odor of diphenylboric acid.

Reaction of $NH_4[B(C_6H_5)_4]$ with methyl alcohol. 3.36 g (0.01 mole) of ammonium tetraphenylborate was heated with 20 ml of anhydrous methyl alcohol in a sealed tube in a boiling water bath for 5 hours. At the end of the heating, the precipitate had disappeared, and a clear solution of a yellowish color had formed. The tube was opened and the liquid volume (25 ml) was measured; 1 ml of solution was removed, in which the ammonia content was determined by titration with hydrochloric acid (2.4 ml of 0.1 N HCl was consumed by 1 ml of solution). The total quantity of ammonia liberated during the reaction was 0.102 g (0.006 mole), which corresponds to a 60% decomposition of the complex. The solvent was distilled. On dilution of the first 10 ml of the solution, 0.8 g of benzene (theoretical yield, by calculation for one phenyl group) was separated.

After removal of the solvent the residue was washed with hot water, dried and weighed. It melted at 212-214° (sintering began at 203°) after recrystallization from hot benzene. The nitrogen content corresponded to triphenylboron ammoniate.

Found %: N 5.30, 5.59. $C_{18}H_{18}BN$. Calculated %: N 5.42.

1 g of the ammoniate was separated, which corresponds to a 38% decomposition of the complex to benzene and the ammoniate.

After separation of the ammoniate, phenol was found in the aqueous filtrate, and identified as the tribromophenol with a m.p. of 92°. 1.9 g of the product was obtained.

The reaction of $K[B(C_6H_5)_3C_{10}H_7]$ with the monoethyl ether of ethylene glycol. 3 g (0.006 mole) of potassium triphenylnaphthylborate was dissolved in 100 ml of the monoethyl ether of ethylene glycol, and was heated at boiling for 2 hours. At the end of the heating the dark-brown solution had an alkaline reaction to litmus. The solvent was distilled. From the residue after steam-distillation, 0.6 g (0.005 mole) of naphthalene, with a m.p. of 80°, was separated. The presence of phenol in the water residue was demonstrated by its reaction with bromine. 0.3 g of tribromophenol with a m.p. of 92° was separated, without a melting point depression in a test of a mixture with the pure substance.

Reaction of $NH_4[B(C_6H_5)_3C_{10}H_7]$ with the monoethyl ether of ethylene glycol. 3 g (0.008 mole) of ammonium triphenylnaphthylborate was dissolved in a mixture of 75 ml of the monoethyl ether of ethylene glycol and 25 ml of water. The mixture was heated for 5 hours in a flask with a reflux condenser. At the end of the heating, the solution in the flask had acquired a brown color. After removal of most of the monoethyl ether of ethylene glycol and the water, the residue was steam-distilled. 1 g (0.0077 mole) of naphthalene with a m.p. of 80° was obtained, without a depression with pure naphthalene.

In the flask (after removal of the naphthalene) on cooling, a crystalline precipitate which was highly soluble in methanol, separated. The precipitate, recrystallized from benzene and washed with anhydrous ether, consisted of 1.1 g (0.0042 mole) of light-weight, snow-white needles with a m.p. of 212-214°. An analysis confirmed the formation of triphenylboron ammoniate.

Found %: N 5.54. $C_{18}H_{18}BN$. Calculated %: N 5.42.

After separation of the ammoniate, phenol was determined qualitatively in the aqueous filtrate as tribromophenol with a m.p. of 93°.

Reaction of $K[B(C_6H_5)_3C_6H_4CH_3]$ with the monoethyl ether of ethylene glycol. A solution of 3.33 g (0.009 mole) of potassium triphenyltolylborate in a mixture of 70 ml of the monoethyl ether of ethylene glycol and 30 ml of water, was heated for 6 hours in a flask with a reflux condenser. The solvent was removed. The first portion of the distillate was diluted with water, and 0.8 g (0.0087 mole), or 96% of the theoretical yield of toluene, was separated. For identification, the toluene was oxidized by an alkaline solution of permanganate. The resulting benzoic acid melted at 121° without a depression with known, pure benzoic acid.

After removal of the solvent and toluene, phenol was determined in the reaction mixture (by conversion to tribromophenol with a m.p. of 93°).

Reaction of $K[B(C_{10}H_7)_3C_6H_5]$ with the monoethyl ether of ethylene glycol. 4.8 g (0.0095 mole) of the complex was dissolved in a mixture of 80 ml of the monoethyl ether of ethylene glycol and 20 ml of water. The mixture was heated at boiling for 4 hours. At the end of the heating, the solution was a dark-brown color. The medium was alkaline. By steam-distillation, 2.5 g (0.0195 mole) of naphthalene with a m.p. of 80° was separated from the reaction mixture, without a depression with the pure substance which corresponded to the breaking away of two naphthyl groups.

The aqueous solution in the flask (after separation of the naphthalene) was evaporated and acidified with sulfuric acid. On cooling, a small quantity of phenylboric acid was separated. The latter was converted to the anhydride by long drying in the air. A test of a mixture with the anhydride of phenylboric acid gave no depression (190°).

Reaction of $K[B(C_6H_5)_4]$ with bromine. A solution of bromine in methanol was introduced dropwise into a suspension of 3.5 g (0.01 mole) of potassium tetraphenylborate in 25 ml of anhydrous methanol, with stirring. In proportion to the addition of bromine, the precipitate of the complex dissolved, with simultaneous disappearance of the bromine color. In all, 8 ml of a 1.25 M solution of bromine, or 1.6 g of bromine (0.01 mole) was introduced. The alcohol was removed. A layer of bromobenzene in a quantity of 1.5 g (0.01 mole) separated on dilution of the residue with water. For identification, the bromobenzene was nitrated to 1,2,4-bromodinitrobenzene. A test sample of a mixture of the resulting nitro product with pure 1,2,4-bromodinitrobenzene had a m.p. of 59°.

After removal of the alcohol and the bromobenzene the residue was steam-distilled. 1 g (0.0065 mole) of biphenyl with a m.p. of 68° was distilled. A test sample of a mixture with pure biphenyl had a m.p. of 70°. The aqueous solution from the steam-distillation flask was evaporated in vacuo at 50-60°. On cooling, 1 g (0.0083 mole) of phenylboric acid crystallized. Its m.p. was 190° (if heating of the capillary was begun in cold sulfuric acid); on the heated sulfuric acid bath it melted with pure phenylboric acid at 214-216° without a depression.

Reaction of $Li[B(C_6H_5)_3C_6H_4CH_3]$ with bromine. A 0.16 M solution of bromine was introduced dropwise into a solution of 2.6 g (0.0077 mole) of lithium triphenyltolylborate in 50 ml of water. The bromine was added until the appearance of a pale-yellow color. In all, 45 ml of bromine water, or 1.2 g (0.0075 mole) of bromine was added. p-Bromotoluene was steam-distilled from the reaction flask. p-Bromobenzoic acid, m.p. 251°, was obtained by the oxidation of p bromotoluene with permanganate. A test sample of a mixture with pure p-bromobenzoic acid melted without a depression. In all, 1.1 g (0.006 mole) of p-bromotoluene separated, which amounted to 80% of the theoretical yield. A small quantity of biphenyl with a m.p. of 70° separated on distillation of the bromotoluene. After separation of the bromotoluene and biphenyl, the presence of a dark, viscous liquid with the characteristic odor of diphenylboric acid was observed in the residue.

Photoreaction of $K[B(C_6H_5)_4]$ with chloroform. 3.5 g of potassium tetraphenylborate and 30 ml of chloroform was exposed for 100 hours. The precipitate of the unreacted complex was filtered off. The chloroform was removed. In the distillate, 0.2 g of m-dinitrobenzene with a m.p. of 90° was separated by nitration, and a test sample of a mixture with pure m-dinitrobenzene melted without a depression. After removal of the chloroform the residue was steam-distilled. 0.3 g of biphenyl with a m.p. of 70°, without a depression with the pure substance, separated. The presence of phenol was demonstrated in the aqueous distillate by its reaction with bromine. KCl was found in the precipitate of the unreacted complex.

Reaction of $K[B(C_6H_5)_4]$ with $FeCl_3$. A solution of 7.3 g (0.045 mole) of anhydrous $FeCl_3$ in 20 ml of acetone was added rapidly to a solution of 4 g (0.011 mole) of potassium tetraphenylborate in 100 ml of dry acetone. The mixture was heated on the water bath for 30 minutes. Then the solvent was distilled off. On dilution of the distillate with water, drops of benzene separated on the surface, which were extracted with carbon tetrachloride and nitrated. 1.2 g of m-dinitrobenzene (64% on the basis of one phenyl), with a m.p. of 90°, separated. A test sample of a mixture with the pure nitro product had a m.p. of 90°.

After separation of the acetone and benzene the residue was steam-distilled. 1.3 g of biphenyl, 75.5% by calculation for 2 phenyls, m.p. of 70°, distilled. A test sample of a mixture with pure biphenyl melted at 70°. After the steam-distillation there was a strongly acid reaction in the residue. The reaction for Fe^{++} was positive. In the aqueous filtrate Fe^{+++} was precipitated as the hydroxide and filtered off. The filtrate was evaporated in vacuo (50-60°) and acidified with H_2SO_4 to an acid reaction to Congo. On cooling, white crystals of phenylboric acid precipitated. Their m.p. was 190° (in a heated bath).

SUMMARY

1. Lithium ethyltriphenylborate and lithium methyltrinaphthylborate, obtained by the usual method in aqueous solutions, were symmetrized. The fresh solutions gave no precipitates with K and NH_4 cations; on standing of the solutions, difficultly soluble tetraphenylborates or tetranaphthylborates of potassium and ammonia formed.

2. On heating of the complex compounds in a solution of the monoethyl ether of ethylene glycol, their decomposition took place with the breaking away of one radical from the anion which, taking up hydrogen from the solvent, gave a hydrocarbon. It was shown that, compared with phenyl, p-tolyl- or α-naphthyl- radicals broke away first on decomposition of the $[B(C_6H_5)_3C_6H_4CH_3]$ or $[B(C_6H_5)_3C_{10}H_7]$ anions.

3. On exposure of chloroform solutions of the tetraphenylborates to ultraviolet light, the breaking away of the phenyl radical resulted which, taking up hydrogen from the chloroform, formed benzene.

4. Bromobenzene, triphenylboron and potassium bromide were formed by the action of bromine on potassium

tetraphenylborate. On reaction of bromine with lithium triphenyltolylborate, the tolyl radical broke away.

5. By the action of ferric chloride on an acetone solution of lithium tetraphenylborate, lithium chloride, biphenyl, phenylboric acid (after treatment with water) and benzene formed, due to the breaking away of hydrogen from acetone by the phenyl radical.

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STUDY OF THE REACTION RATE OF THE FORMATION OF l-ASCORBIC ACID FROM THE HYDRATE OF DIACETONE-2-KETO-l-GULONIC ACID IN AN AQUEOUS MEDIUM

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The conversion of 2-keto-l-gulonic acid and its acetonized derivative, the hydrate of diacetone-2-keto-l-gulonic acid, to l-ascorbic acid, is the subject of numerous investigations. The reaction may be carried out under different conditions: with and without catalysts, without a solvent, in an aqueous solution, in a medium of organic solvents, etc. (reviews [1, 2]). In spite of the presence of numerous works and patents in this field, the theory of the process is still inadequately developed with respect to the conditions of carrying out the reaction. Berezovsky and Strelchunas [3] investigated in detail the course of the reaction in a medium of an inert organic solvent, under the influence of hydrogen chloride in the presence of alcohols, and interpreted the chemism of the process.

There is much less data on the course of the reaction in an aqueous medium. Yet Reichstein and Grüssner [4] found that on heating with water at 100°, 12.7% of the 2-keto-l-gulonic acid was converted to ascorbic acid after 2 hours. The reaction proceeded with a higher yield at 120-140° under pressure [5, 6].

Reichstein and Grüssner showed that the reaction is accelerated considerably by the addition of acids; a 27% yield of ascorbic acid was obtained after 4 hours in a 0.2 N solution of HCl at 100°. They found that on prolonged action, hydrochloric acid decomposed the ascorbic acid [4]. Hirst and his coworkers showed that furaldehyde and its polymers are formed by the decomposition of ascorbic acid under these conditions [7]. There are numerous patents on the production of l-ascorbic acid in the presence of different acids (review [2]).

The kinetics of the conversion of 2-keto-l-gulonic acid to ascorbic acid in an aqueous medium was studied in detail by Regna and Caldwell [8]. The reaction was investigated under the following conditions: the HCl concentration in the reaction mixture amounted to 5 moles/liter, the initial concentration of 2-keto-l-gulonic acid amounted to 0.05 mole/liter, and the temperature was 59.9° and 69.9° (± 0.02°). The previously established scheme of the course of the process studied was confirmed kinetically by Regna and Caldwell:

$$\text{2-keto-l-gulonic acid} \xrightarrow[\text{(I)}]{K_1} \text{l-ascorbic acid} \xrightarrow[\text{(II)}]{K_2} \begin{array}{l}\text{decomposition}\\ \text{products of}\\ \text{l-ascorbic acid}\end{array} \xrightarrow[\text{(III)}]{K_3} \text{polymers}$$

They determined the rate constants of the reactions of formation of l-ascorbic acid (K_1) and of its decomposition (K_2) as consecutive reactions of the first order ($K_1 = 2.5 \cdot 10^{-3}$ and $8.2 \cdot 10^{-3}$, $K_2 = 4.9 \cdot 10^{-4}$ and $14.1 \cdot 10^{-4}$ at 59.9 and 69.9°, respectively. On the basis of the values of K_1 and K_2 the potential maximum yields of l-ascorbic acid were calculated, which were confirmed experimentally. At 59.9° the maximum yield amounted to 67.6%, and at 69.9° it was 69.9% of the theoretically possible yield.

The study of the reaction rate of the formation of l-ascorbic acid (AA), by heating the hydrate of diacetone-2-keto-l-gulonic acid (HDAKGA) with concentrated hydrochloric acid, was the problem of the present work. We studied systems, unlike Regna and Caldwell's experiments, with high organic acid contents (2-2.5 moles/liter), but with a similar hydrogen chloride content in the system (~5 moles/liter); moreover, our systems contained acetone, which formed on hydrolysis of the HDAKGA. This presented the possibility of judging whether a change of composition of the mixture (increased organic acids content, presence of acetone, decreased quantity of water, with the same catalyst content), and whether replacement of 2-keto-l-gulonic acid by its diacetone derivative, would affect the rate of the process. Since it is known that in an acid medium the cleavage of acetone and the formation of 2-keto-l-gulonic acid proceeds extremely rapidly [4], this latter condition could seem unessential at first sight.

At the same time, kinetic data would enable us to judge the mechanism of the reaction, to establish the presence or absence of parallel side reactions of the decomposition of HDAKGA or of its conversion to other products (IV), under the conditions studied:

$$\begin{tikzcd}
\text{HDAKGA} \arrow[r, "\text{(I)}"'] \arrow[d, "\text{(IV)}"] & \text{AK} \arrow[r, "\text{(II)}"'] & \underset{\text{(furfurol)}}{\text{decomposition products AK}} \arrow[r, "\text{(III)}"'] & \text{polymers} \\
\text{Decomposition products or conversion of HDAKGA} & & &
\end{tikzcd}$$

The investigation included the conduction of two series of experiments: the rate of accumulation of AA in the reaction mixture, and parallel with it, the rate of decomposition of AA ,were determined under similar conditions. The constants of the reaction of formation of AA (k_1) and the decomposition of AA (k_2) were calculated on the basis of the data obtained. This method, used by Regna and Caldwell before us, was the most logical, since there was no suitable method for direct determination of the 2-keto-l-gulonic acid in the reaction mixtures.

EXPERIMENTAL*

General Method. Measurement of the reaction rates was carried out by heating samples of the reaction mixtures with definite ratios of components in sealed test tubes, which were placed in a water thermostat with an accuracy of temperature regulation of ±0.1°. After a definite time, the tubes were removed from the thermostat and cooled with cold water, after which the determination of the ascorbic acid content was carried out at once by titration with iodine, with the use of starch as an indicator. The investigation was carried out at 60 and at 70° (±0.1°), with different ratios between the quantities of the hydrate of diacetone-2-keto-l-gulonic acid (or ascorbic acid) and the hydrochloric acid concentration. An experiment was carried out at 50° for comparison.

Preparation of the reaction mixtures. HDAKGA – hydrochloric acid mixtures. I. HDAKGA: hydrochloric acid ratio = 1.575 g of HDAKGA per 1 ml of concentrated hydrochloric acid (2.06 moles of HCl per mole of HDAKGA). The hydrogen chloride content in this mixture amounted to ~4.9 moles per 1 liter of the mixture.

II. HDAKGA: hydrochloric acid ratio = 2.39 g of HDAKGA per 1 ml of concentrated hydrochloric acid (1.36 moles of HCl per 1 mole of HDAKGA). The hydrogen chloride content in the reaction mixture amounted to ~3.7 moles per 1 liter of the mixture.

AA – hydrochloric acid – acetone mixtures. Mixtures for determination of k_2 (the rate constant of the decomposition of ascorbic acid) were prepared by mixing weighed portions of AA with acetone and concentrated hydrochloric acid. The acetone was added in a quantity of 2 moles per 1 mole of AA (according to the equation of the hydrolysis reaction of HDAKGA); hydrochloric acid was added in the same ratios, at which it occurred in mixtures with equivalent quantities of HDAKGA.

Starting materials: the hydrate of diacetone-2-keto-l-gulonic acid had a content of 92.4%, based on the anhydrous substance, or 98.5% based on the hydrated molecule. Recrystallized, medicinal l-ascorbic acid contained 99.2%, by iodine. The chemically pure hydrochloric acid contained 11.15 moles/liter of HCl.

Calculation of the reaction rate constants. Calculation of k_2, the rate constant of the decomposition of AA, was made by the usual formula of a first order reaction:

$$k_2 = \frac{2.303}{t} \log \frac{C_0}{C}. \tag{1}$$

For calculation of k_1, the rate of formation of AK, it is possible to use Formula (2), obtained by transformation of the Rakovsky formula for the determination of the content of the intermediate substance in a consecutive reaction of the first order [9, 10], which is identical with the formula used by Regna and Caldwell [8].

$$k_1 = -\frac{1}{0.4343\,t} \log \left[e^{-k_2 t} - \frac{b}{a_0} \frac{k_1 - k_2}{k_1} \right]. \tag{2}$$

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* M. F. Galina and M. P. Benyamin participated in conduction of the experimental part of the work.

Since, according to our data $k_1 \gg k_2$ (by approximately 100 times), we calculated the value of k_1 by simplified Formula (3)

$$k_1 = -\frac{\log\left[e^{-k_2 t} - \frac{b}{a_0}\right]}{0.4343\,t} \tag{3}$$

where a_0 is the content of the initial substance (HDAKGA) and $\underline{b}$ is the content of ascorbic acid at time $\underline{t}$.

The maximum possible yield of AA was calculated by the formula [8, 10],

$$\left(\frac{b}{a_0}\right)_{\text{max.}} = \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}} \tag{4}$$

The time necessary for attainment of the maximum yield $t_{\text{max.}}$ [9], was determined by the formula

$$t_{\text{max.}} = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2} \tag{5}$$

Discussion of Results

The experimental data on the determination of the AA content in reaction mixtures, in relation to the time at different temperatures and ratios of components, are cited in Figs. 1 and 2. As a result of the fact that the decomposition of AA proceeded to a negligible extent under the conditions studied, the curves of Fig. 2 approximate straight lines.

On the basis of the experimental data, the values of the constants of the reaction of formation of AA (k_1) and of the reaction of its decomposition (k_2), were calculated by Formulas (1) and (3) at 60 and 70°. The values of k_1 and k_2 were characterized by satisfactory constancy over the entire time interval, from the beginning of the reaction until the attainment of the maximum yield. A scattering of the values of k_1 and k_2 was observed in parallel experiments, and in experiments with different period of heating which can be explained by the viscous consistency of the reaction mixtures. Data illustrating the resulting values of k_1 and k_2 for two parallel experiments are cited in Table 1.

TABLE 1

Time (in min.)	$k_1 \cdot 10^2$ at 60° (HCl: HDAKGA = 1.36	Time (in min.)	$k_2 \cdot 10^4$ at 60° (HCl: AA = 1.36)
60	1.1, 1.1	300	1.3, 1.0
90	0.9, 0.9	360	0.8, 1.1
120	0.9, 1.1	480	1.2, 0.6
150	1.2, 1.0	540	0.9, 1.0
180	0.9, 0.9	600	0.8 –
210	0.8, 1.0		
240	0.9, 0.9		

TABLE 2

Temperature	Initial molar ratio of $\frac{\text{HCl}}{\text{HDAKGA}}$ (or $\frac{\text{HCl}}{\text{AA}}$)	Average value of $k_1 \cdot 10^2$	Average value of $k_2 \cdot 10^4$	Calculated maximum yield of AA (in %)	Calculated time of attainment of the maximum yield (min.)
60°	2.06	1.2	1.5	95.0	342
60	1.36	1.0	0.9	95.9	468
70	2.06	2.7	6.4	91.5	136

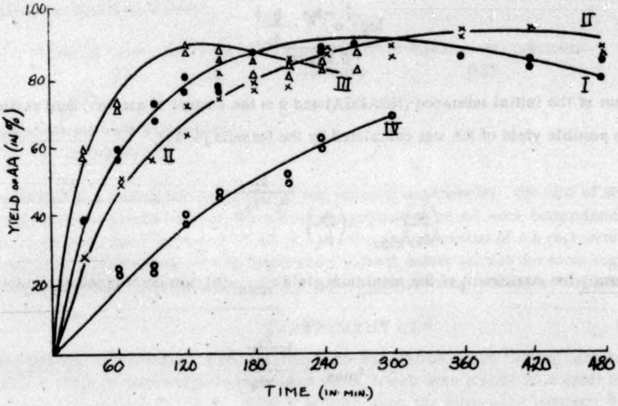

Fig. 1. Relation of ascorbic acid yield to the temperature and composition of the mixture.
A) Yield of AA (in %); B) time (in min.).
I) 60°, 2.06 moles HCl per 1 mole of HDAKGA; II) 60°, 1.36 moles of HCl per 1 mole of HDAKGA; III) 70°, 206 moles of HCl per 1 mole of HDAKGA; IV) 50°, 1.36 mole of HCl per 1 mole of HDAKGA.

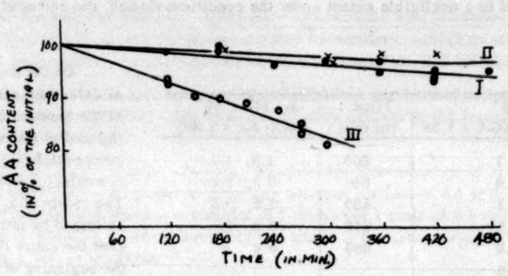

Fig. 2. Relation of the rate of decomposition of ascorbic acid to the temperature and composition of the mixture.
A) AA content (in % of the initial); B) time (in min.).
I) 60°, 2.06 moles of HCl, 2 moles of acetone per 1 mole of AA; II) 60°, 1.36 moles of HCl, 2 moles of acetone per 1 mole of AA; III) 70°, 2.06 moles of HCl, 2 moles of acetone per 1 mole AA.

On the basis of the resulting values of k_1 and k_2, the maximum yields of AA (in molar percentages of the initial quantity of HDAKGA) and the time necessary for attainment of the maximum yield ($t_{max.}$) were calculated. The data obtained are cited in Table 2.

It is seen from a comparison of the data of Table 2 and Fig. 1 that the calculated values of the maximum yield of AA and the times of attainment of the maximum yield agree with those found experimentally. Hence, it is evident that the constant k_1, found for the quantity of AA which formed and calculated by the Rakovsky formula, correctly express the course of the reaction. Therefore, the process is a consecutive reaction of the first order under the conditions studied. It can be predicted on the basis of the data obtained, that parallel reactions of decomposition of HDAKGA will not take place in practice.

Under the conditions investigated, the decomposition of ascorbic acid increases sharply with an increase of temperature (by about 4 times in the interval from 60 to 70°). The rate of conversion of HDAKGA to AA also increased, but to a smaller degree (approximately by 2 times in the temperature interval indicated); therefore, with an increase of temperature, the overall process of accumulation of ascorbic acid in the reaction mixture has a tendency to decrease.

In connection with this, and also in connection with the increase of the absolute rate of the reaction, the time required for attainment of the maximum yield decreases sharply with an increase of temperature (approximately from 6 hours at 60° to 2 hours at 70°). The rate of the process depends also on the quantity of hydrochloric acid in the mixture. The rate of decomposition of ascorbic acid decreases somewhat with a decrease of the quantity of hydrochloric acid supplied per unit weight of HDAKGA, under the conditions studied. At the same time, the rate of conversion of HDAKGA to AA drops, which can be explained by the decrease of the hydrogen chloride concentration in the reaction mixture. This fact appears to be useful in the increase of the time necessary for attainment of the maximum yield. Moreover, it is necessary to note that an increase of duration and temperature of the process is accompanied by the formation of a considerable quantity of resin.

A comparison of the values of k_1 and k_2, cited in Table 2 with Regna and Caldwell's data indicated above, showed that under the conditions which we studied, the value of k_1 was 3-5 times larger and the value of k_2 was smaller by a factor of 2-3. This can be explained by a consideration of the different composition of the reaction mixtures cited above, particularly by the small quantity of water in the mixtures which we studied. However, it is not excluded that the rates of conversion of the hydrate of diacetone-2-keto-l-gulonic acid, and of the same 2-keto-l-gulonic acid to ascorbic acid may be different.

SUMMARY

1. The reaction rate of production of l-ascorbic acid from the hydrate of diacetone-2-keto-l-gulonic acid by heating it with concentrated hydrochloric acid was investigated.

2. The rate constants of the formation and of the decomposition of l-ascorbic acid, the maximum potential yields, and the times necessary for attainment of the maximum yield were determined at 60 and 70°.

3. It was shown that a monomolecular consecutive reaction takes place under the conditions studied.

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EFFECT OF METALLIC IONS ON THE PROPERTIES OF ETHYLCELLULOSE

III. RELATION OF THE ELASTO-PLASTIC CHARACTERISTIC OF ETHYLCELLULOSE GELS TO THE SODIUM ION CONTENT IN THEM

S. A. Glikman, O. G. Efremova and V. M. Averyanova

In our previous reports [1] it was shown that the introduction of calcium and iron compounds into ethylcellulose led to an increase of the viscosity of its solutions in non-polar solvents, and led to an increase of all the elasto-plastic properties of its gels. Moreover, very small quantities of these metals, of the order of a hundredth of a per cent by weight of the ethylcellulose, which corresponds to one metal ion per ten monomeric links (glucose radicals), had a strong effect. It is known [2] that usually a small number of carboxyl groups are included in the molecules of industrial samples of ethylcellulose. Apparently, multivalent cations replacing hydrogen in these groups, are bound between the ethylcellulose molecules by an ionic bond, the energy of which is much greater than that of the hydrogen bond. With a relatively small number of ionic bonds forming, of the order of one per molecule of ethylcellulose, the increase of intermolecular cohesion does not lead to an essential change of the structure of the ethylcellulose solutions, even in non-polar solvents; the true solution state is retained, but the average degree of association of the high-polymer molecules increases. In gels where, instead of labile equilibrium associates, there exists a permanent network of polymer molecules connected between themselves at relatively few points, multivalent metallic ions increase the number and stability of these bonds.

There is little information in the literature on the effect of univalent metallic ions on the properties of the cellulose esters; moreover, the results obtained by different authors are contradictory. Thus, for example, Drinberg [3] observed a strong decrease of the viscosity of nitrocellulose and acetylcellulose solutions on introduction of sodium acetate and palmitate. Meanwhile, Glickman, Mindlin, Guseva and Zeldovich [4] showed that treatment of nitrocellulose by solutions of sodium carbonate led to an increase of the viscosity of its solutions. Relative to ethylcellulose, Evans and Spurlin [2] found that treatment with sodium carbonate led to an increase of the viscosity of its benzene solutions.

Although sodium is an inevitable component of the ash of industrial ethycellulose samples, its effect on the mechanical properties of ethylcellulose and the gels formed by it have not been studied until now.

Objects of investigation and their preparation. Three samples of ethylcellulose, the characteristics of which are cited in Table 1, served as the material for our investigation. Samples 348 and 424 were not studied in the original condition. They were partially decalcified by repeated reprecipitation from acetone-water solutions containing 0.2% HCl, followed by a careful washing out of the Cl^- ions. The ash obtained after combustion of the decalcified preparations contained chiefly SiO_2 and traces of iron and sodium.

TABLE 1

Characteristics of Ethylcellulose Samples

Sample	Ethoxyl number (in %)	Ash content (in %)		Intrinsic viscosity [η] in a mixture of alcohol and benzene	K'
		in original preparation	after treatment		
224	48.0	0.27	–	1.74	0.65
348	46.5	0.36	0.09	2.14	0.48
424	46.4	0.40	0.18	1.66	0.29

For introduction of sodium ions into an 8% solution of ethylcellulose in acetone, a 2% aqueous solution of NaOH was added in such a quantity that the sodium content amounted to 0.1% by weight of the ethylcellulose. The solution was left for 12 hours, during which from time to time it was stirred. Then the ethylcellulose was precipitated from the solution by distilled water, the precipitate was filtered off, and the filtrate was evaporated in vacuo at 60°. After evaporation the precipitate was added to the main precipitate and dried to constant weight at 100°. This relieved us of the necessity of controlling the quantity of sodium introduced, since the addition remained completely in the preparation.

Sample 224 and pre-decalcified samples 348 and 424 were subjected to such a treatment. For evaluation of the effect of sodium ions, the preparations thus obtained were compared with those reprecipitated from acetone solutions by distilled water, and Sample 348 was also compared with the preparation treated with a $Ca(OH)_2$ solution by a similar method.

The data on the metallic ion contents in the samples are cited in Table 2.

Viscosity of the dilute solutions. We determined the concentration dependence of the viscosity of solutions of ethylcellulose in a mixture of alcohol with benzene (1 : 4) (Sample 348), and in a mixture of alcohol and toluene (1 : 4) (Sample 424). A viscometer of the standard suspended Ubellohde type was used for determination of the viscosity. The determinations were carried out at a constant temperature (20° ± 0.01° for solutions of 424 and 25° ± 0.01° for solutions of 348). The resulting data are presented in Fig. 1.

TABLE 2

Sample	Ash content (in %)	Content of metals by weight of ethylcellulose (in %)		
		Na	Ca	Fe
224 (original)	0.27	not determined	0.090	0.030
224, treated with $Ca(OH)_2$	0.37	not determined	0.190	0.030
224, treated with NaOH	0.37	0.10 introduced	0.090	0.030
348, decalcified	0.09	traces	0.001	0.007
348, treated with $Ca(OH)_2$	0.19	traces	0.100	0.007
348, treated with NaOH	0.19	0.10	0.001	0.007
424, decalcified	0.18	traces	traces	traces
424, treated with NaOH	0.28	0.10	traces	traces

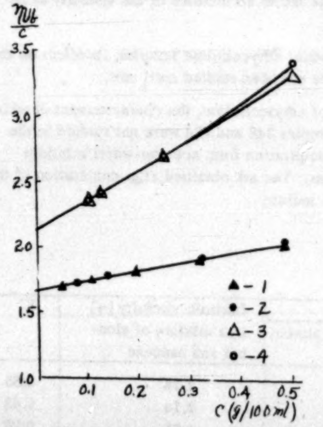


Fig. 1. Effect of treatment with alkali on the viscosity of solutions of ethylcellulose in a mixture of alcohol and benzene.
1) Sample 424, treated with NaOH; 2) sample 424, decalcified; 3) sample 348, treated with NaOH; 4) sample 348, decalcified.

It is evident from the figure that the introduction of small quantities of sodium into the composition of the ethylcellulose was not reflected by the viscosities of its dilute solutions (0.5% and less) in both mixtures of solvents studied. The values of the intrinsic viscosity and the values of the constants K' also remained unchanged. These results agree with those which we obtained earlier [1] relative to the effect of Ca^{++} ions on the viscosity of solutions of ethylcellulose in a mixture of alcohol and benzene. Obviously, here also the polar solvent of alcohols, highly solvating the carboxyl groups of ethylcellulose, screens them, inhibiting intermolecular interaction.

The elasto-plastic properties of the gels. 8 and 10% gels formed by ethylcellulose with dibutylphthalate served as the object of our investigation. We studied five fundamental characteristics, the meaning of which Rebinder [5] defined as follows:

1. P_k is the elastic limit, i.e., the minimum shear stress at which plastic deformation arises.

2. E_1 is the initial (conditionally-instantaneous) modulus of elasticity. $E_1 = \frac{P}{E_0}$, where P is the shear stress and E_0 is the conditionally-instantaneous deformation (observed in a period of time of less than a second).

3. E_2 is the modulus of elasticity. $E_2 = \frac{P}{E_m - E}$, where $E_m - E_0$ is the highly-elastic deformation developing in time.

4. η_1 intrinsic, i. e., the relaxation viscosity of the gel, which characterizes its flow at extremely small rate gradients, not exceeding the rate of thixotropic regeneration of the structure disturbed by shear: $\eta_1 = \frac{P - P_k}{(d\epsilon/d\tau)_{\text{residual}}}$, where $P - P_k$ is the stress acting, maintaining a stationary flow, and $(d\epsilon/d\tau)_{\text{residual}}$ is the constant rate of this flow, remaining on completion of the development of the elastic deformation.

5. η_2 is the conventional viscosity of the elastic after-effect characterizing the resistance by increase of the highly-elastic deformation during the first conditionally-small period of deformation: $\eta_2 = \frac{P}{(d\epsilon/d\tau)_0 - (d\epsilon/d\tau)_{\text{residual}}}$, where $(d\epsilon/d\tau)_0$ is the initial rate of plastic flow.

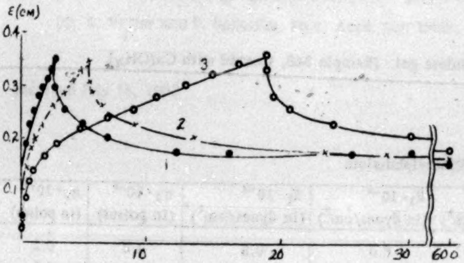


Fig. 2. Kinetics of deformation of 8% ethylcellulose gel. (Sample 348, decalcified).
1) P = 196, 2) P = 143, 3) P = 89 dynes/cm².

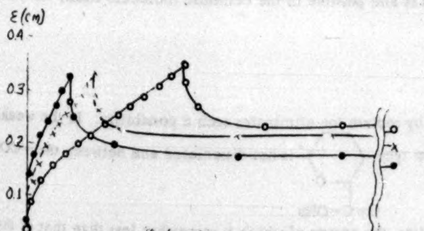
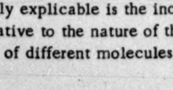


Fig. 3. Kinetics of deformation of 8% ethylcellulose gel. (Sample 348, treated with NaOH).
1) P = 304, 2) P = 250, 3) P = 196 dynes/cm².

For determination of all these constants, we used the method of tangential displacement of layers, developed by Veiler and Rebinder [6], with observance of a series of special conditions which we developed earlier (selected spring, range of stress, consideration of elastic deformation of the gel proceeding under the influence of the weight of the layers, etc.) [1].

The data obtained for one of the samples studied is presented in Figs. 2-4. Similar curves were obtained for the other samples. The values of the elasto-plastic properties found on the basis of these graphs for all of the samples studied are cited in Table 2.

It is seen from these data that the introduction of small quantities of sodium into the composition of ethyl cellulose considerably increased all the elasto-plastic characteristics of the gel. This relation appeared more graphically for the decalcified Samples 348 and 424. For Sample 224 (non-decalcified) this regularity was somewhat extinguished, since the initial preparation with which we compared the samples treated with NaOH, itself contained a certain quantity of metallic ions, commensurate with the additionally introduced ions (see Table 2). However, in general here also the same regularity appears, i. e., sodium ion considerably increases the elasto-plastic characteristics of the gels. The experiments made with Sample 348, treated with $Ca(OH)_2$, showed that calcium ion increases the elasto-plastic properties of the gels to a greater degree than does sodium ion (Table 3). We see that the stability, hardness and viscosity of the gels are found to be highest in the presence of calcium ions. This is explained certainly by the formation of a few bridge bonds of the  $-\underset{\underset{O}{\|}}{C}-O-Ca-O-\underset{\underset{O}{\|}}{C}-$, type between the ethylcellulose molecules.

More difficultly explicable is the increase of the elasto-viscous characteristics of the gels under the influence of sodium ions. Relative to the nature of this phenomenon the following assumption may be stated. Between the free carboxyl groups of different molecules of cellulose ester, the formation of hydrogen bonds is possible, which,

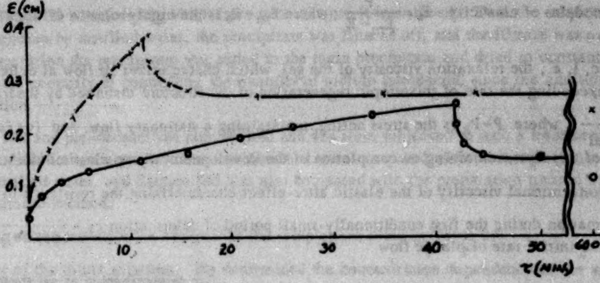
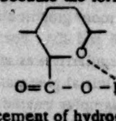


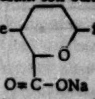
Fig. 4. Kinetics of deformation of 8% ethylcellulose gel. [Sample 348, treated with $Ca(OH)_2$]. 1) P = 2080, 2) P = 1363 dynes/cm^2.

TABLE 3

Elasto-plastic Characteristics of Ethylcellulose Gels in Dibutylphthalate

Sample	Concentration of gel (in %)	P_k (in dynes/cm^2)	$E_1 \cdot 10^{-3}$ (in dynes/cm^2)	$E_2 \cdot 10^{-3}$ (in dynes/cm^2)	$\eta_1 \cdot 10^{-5}$ (in poises)	$\eta_2 \cdot 10^{-6}$ (in poises)
224, original	10.0	160	6.0	0.8	4.2	0.2
224, treated with NaOH	10.0	200	18.0	0.9	20.0	0.5
424, decalcified	10.0	240	6.5	1.3	3.3	0.2
424, treated with NaOH	10.0	610	18.0	4.2	5.6	0.8
348, decalcified	8.0	60	3.7	0.4	1.7	0.5
348, treated with NaOH	8.0	100	6.5	1.0	2.4	0.8
348, treated with $Ca(OH)_2$	8.0	1250	31.0	12.5	26.0	–

of course, strengthen the gel structure. But not all the carboxyl groups of the cellulose molecules by far are found to be mutually bound, because the formation of a hydrogen bond is also possible in the cellulose molecule itself, for example, according to the 

The replacement of hydrogen in the carboxyl group by sodium ion eliminates such a possibility. In the weakly solvated cellulose ester the solvent or the gel of the sodium type 

is not dissociated and between the −COONa dipoles of the adjacent molecules an electrostatic bond arises, the energy of which is somewhat less than that of the hydrogen bond; meanwhile, the number of such bonds appears more significant because, as observed above, the hydrogen bonds can also form inside the cellulose molecule.

SUMMARY

1. It was found that introduction into ethylcellulose of Na^+ ions in the quantity of 0.1% by weight of the ethylcellulose is not reflected by the viscosity of the dilute solutions in mixtures of alcohol with benzene and alcohol with toluene.

2. It was found that all the elasto-plastic characteristics (elastic limit, modulus of elasticity and viscosity) of 8-10% gels of ethylcellulose with dibutylphthalate increased on introduction of 0.1% Na^+ into the ethylcellulose. The Ca^{++} ion increased these characteristics more than did Na^+ ion.

3. A hypothetical explanation for the regularities found for the action of sodium ions on the elasto-plastic characteristics of the gels was given.

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INVESTIGATIONS IN THE FIELD OF QUINONES

II. SYNTHESIS OF CHLORO- AND BROMO-SUBSTITUTED HYDROQUINONES BY THE ACTION OF ETHER SOLUTIONS OF HYDROGEN CHLORIDE AND BROMIDE ON QUINONES

A. P. Terentyev, A. N. Grinev and A. B. Terentyev

In 1844 Wöhler [1], studying the properties of p-benzoquinone, found that the latter was converted to chlorohydroquinone by heating with concentrated hydrochloric acid. However, as was found later [2], the production of chlorohydroquinone by this method is associated with a number of complications: part of the substance undergoes resinification, and together with the chlorohydroquinone, hydroquinones containing more than one chlorine atom formed. According to a different method, the reaction between quinone and hydrogen chloride was carried out at room temperature in a solution of chloroform [2, 3] or carbon tetrachloride [4]. This method, used recently for production of a series of chlorohydroquinones (75% yield) is unsatisfactory, because of the length of the reaction and the relatively poor solubility of quinones in chloroform [5]. The chlorination of hydroquinone leads usually to a mixture of 2,3- and 2,5-dichlorohydroquinones [6, 7].

The reaction of p-benzoquinone with concentrated hydrobromic acid or hydrogen bromide in chloroform leads to the formation of a mixture of bromohydroquinone and 2,5-dibromohydroquinone [8, 9]. Thus, until recently a satisfactory method of production of chloro- and bromohydroquinones had not been described fully. It can be assumed that, because of their strong polarization, hydrogen halide molecules will be added more rapidly to the quinone molecule in ether or dioxane solutions, excluding the occurrence of side reactions. As a result of testing this assumption, we developed a method of production of chloro- and bromohydroquinones, according to which the quinone is introduced into reaction with a previously prepared solution of hydrogen chloride or bromide in ether or dioxane. The reaction proceeds quantitatively in 30-40 minutes and requires no strong dilution.

EXPERIMENTAL

1. Production of chlorohydroquinone. 100 g of p-benzoquinone was added in 30-40 minutes by portions at the rate of 5-10 g to ether (200 g) saturated at 0° with hydrogen chloride * (50 g), with cooling and stirring.

The introduction of new portions was carried out only after decolorization of the ether solution. In the flask after distillation of the ether, pure chlorohydroquinone crystallized with a m.p. of 105°, which corresponded to the literature value [2, 3]. The yield was 133 g (quantitative).

If 30 g of p-benzoquinone is added to the ether distillate containing hydrogen chloride, an additional 39.5 g of chlorohydroquinone can be obtained.

2. Production of dichlorohydroquinone. We carried out the reaction just as indicated above, but because of the poorer solubility of dichlorohydroquinone in ether, a larger quantity of ether was used.

100 g of ether, 31 g of hydrogen chloride and 30 g of chloroquinone were used for the experiment. The yield of dichlorohydroquinone (quantitative) was 37.5 g. To the distillate 20 g of quinone was added, and 25 g of dichlorohydroquinone was obtained. The dichlorohydroquinone had a m.p. of 120-128°. 2,6-Dichlorohydroquinone, m.p. 162-163° (m.p. of the quinone 121°), and 2,5-dichlorohydroquinone, m.p. 166-167° (m.p. of quinone 160.5-162°), were obtained by recrystallization from acetic acid and petroleum ether. The melting points corresponded to the literature values [3].

The dichlorohydroquinone with a m.p. of 120-128°, from which we separated 2,5- and 2,6-dichlorohydroquinone, was oxidized to quinone, and by the addition of hydrogen chloride to the latter, trichlorohydroquinone

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* An excess of hydrogen chloride of not less than 1/3 of the quantity required by the equation of the reaction was used in the reaction.

with a m.p. of 135°, which corresponded to the literature value [3], was obtained.

3. Production of bromohydroquinone. The reaction was carried out just as in the above-described instances, 50 g of ether, 32 g of hydrogen bromide, and 35 g of p-benzoquinone were used in the experiments. The yield of the bromohydroquinone was 43.5 g (quantitative). Its m.p. was 112-113°, which corresponded to the literature value [9].

The results of all the experiments carried out are recorded in the Table.

Initial quinone	Hydrogen halide	Hydroquinone obtained	Yield	Melting point		Comment
				of substance obtained	literature value	
p-benzoquinone	HCl	chlorohydroquinone	Quantitative	105°	106° [2, 3]	
tolylquinone	HCl	4-chlorotolylhydroquinone	Quantitative	175	175–176 [10]	Isomers separated by recrystallization from petroleum ether
		3-chlorotolylhydroquinone	Quantitative	115–116	115 [11]	
chloro-p-benzoquinone	HCl	2,5-dichlorohydroquinone	Quantitative	166–167	166 [3]	Isomers separated by recrystallization from acetic acid and petroleum ether
		2,6-dichlorohydroquinone	Quantitative	162–163	161 [3]	
dichloroquinone (mixture of isomers)	HCl	trichlorohydroquinone	Quantitative	135	136 [3]	
p-benzoquinone	HBr	bromohydroquinone	Quantitative	112.5	110–111 [9]	
tolylquinone	HBr	4-bromotolylhydroquinone	92%	176	179 [12]	Separated by recrystallization from benzene
bromo-p-benzoquinone	HBr	2,6-dibromohydroquinone	94%	166–167	164 [13]	Separated by recrystallization from benzene
dibromoquinone	HBr	tribromohydroquinone	Quantitative	135	136 [9]	

SUMMARY

A convenient method of production of chloro- and bromohydroquinones by the reaction of quinones with ether solutions of hydrogen chloride and bromide was developed.

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THE NITRATION OF 1,1-DIPHENYLETHANE

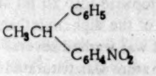
I. P. Tsukervanik and M. D. Sokolnikova

The nitro derivatives of diarylethanes recently have attracted attention to themselves as possible insecticides of the DDT type [1] and as raw material for the synthesis of therapeutic preparations [2]. The nitration of chlorinated diarylethanes, $CCl_3CH(AR)_2$, and the reduction forming dinitro compounds, have been studied [3].

The work was begun [4] by nitration of 1,1-diphenylethane in connection with a simple method found for synthesis of the diarylethanes from acetylene and aromatic compounds [5]. Only recently a report has appeared on the nitration of the aromatic nucleus of diphenylethane. Benoit and Eliopoulo [2] obtained small yields of dinitro- and tetranitrodiphenylethanes. A synthesis of mononitrodiphenylethane by means of copper nitrate was proposed in a patent [6].

Konovalov and Yatsevich [7] studied the nitration of the side chain of 1,1-diphenylethane with dilute nitric acid; they demonstrated the formation of diphenylnitroethanol, which is readily converted to diphenylnitroethylene. By these results, the inaccuracy of Anschütz and Römig's earlier works [8] was established, in which the structure of the ester of nitric acid was attributed to the nitration product. Much later, Wieland [9], and also Anscütz [10] confirmed the data of Konovalov and Yatsevich; however, they did not refer to their work. In these new works on the nitration of the side chain of diphenylethane, diphenyldinitroethylene was also described as a product of the action of nitric acid on diphenylethylene.

Thus, the feasibility of production of the following nitro derivatives of 1,1-diphenylethane is contemplated:



$CH_3CH(C_6H_5)(C_6H_4NO_2)$ (I), $CH_3CH(C_6H_4NO_2)_2$ (II), $CH_3CH[C_6H_3(NO_2)_2]_2$ (III),

$(C_6H_5)_2C(OH)CH_2NO_2$ (IV), $(C_6H_5)_2=CHNO_2$ (V), $(C_6H_5)_2C=C(NO_2)_2$ (VI).

We studied the effect of the conditions of nitration on the structure and yields of the products, striving to find preparative methods for the synthesis of the substances enumerated. We were able to improve on previous results [4] of nitration by fuming nitric acid. On slow addition of 1,1-diphenylethane to a four-fold volume of HNO_3 (d 1.5) at −15°, di-(4-nitrophenyl)-ethane (II) was obtained in a yield of 66% of the theoretical. This same product was obtained in a somewhat smaller yield (50%) in nitration experiments with the usual nitrating mixture at 30-50°. The reactions were carried out by introduction of 1 volume of diphenylethane into a mixture of 4 volumes of HNO_3 (d 1.4) and 6 volumes of H_2SO_4 (d 1.84). If these reactions are carried out by heating the mixture at about 100°, a mixture of the dinitro and tetranitro compound (III) is obtained. A considerable yield (45% of the theoretical) of substance (III) was obtained by the use of a large excess of sulfuric acid (2 volumes of HNO_3 and 5 volumes of H_2SO_4).

4,4'-Dinitrobenzophenone and 2,2',4,4'-tetranitrobenzophenone were obtained by oxidation of the nitration products by chromic anhydride; in the same oxidation a certain quantity of 2,4'-dinitrobenzophenone was obtained from the resinous residue from the nitration products. This gave a basis for assuming that, besides the chief p,p-dinitrodiphenylethane, some o,p-isomer also forms. Similar results were obtained by Staedel [11] on nitration of diphenylmethane.

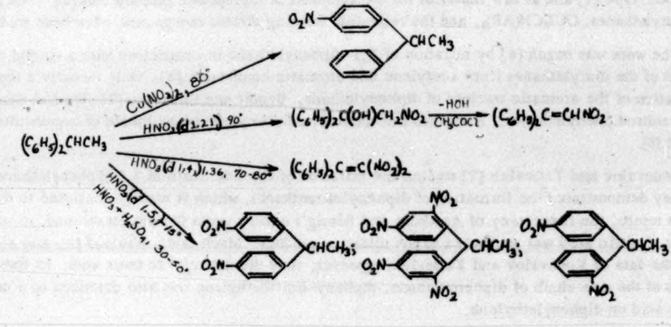
We then proceeded to nitration by means of one volume of nitric acid of different concentrations. In Rinkenbach's work [12] the production of dinitrodibenzyl in a yield of 95% of the theoretical by nitration of dibenzyl with HNO_3 (d 1.42) at 70-80° was described. We repeated this reaction with 1,1-diphenylethane. Instead of product (II), diphenyldinitroethylene (VI) was obtained unexpectedly. The yields of this substance amounted to 80% of the theoretical with somewhat more dilute nitric acid (d 1.365) at 75-80°. On further dilution of the nitric acid, 1,1-diphenyl-1-hydroxy-2-nitroethane (IV) appeared, which became the sole product of the nitration with HNO_3.

(d 1.21) at 80-90° (its yield 53%). Also, in this case, an increase of the reaction temperature to 110° led to accumulation of 1,1-diphenyl-2,2-dinitroethylene (VI).

Thus, we found that the nitration of the side chain of 1,1-diphenylethane proceeds even on heating with concentrated nitric acid. The yields of Substances (IV) and (VI) which we obtained somewhat exceeded those described in the literature [7, 9, 10].

For production of 1-phenyl-1-(4-nitrophenyl)-ethane (I) we used a method described for the nitration of biphenyl [13]. Copper nitrate was added to a solution of 1,1-diphenylethane in acetic anhydride. The mixture was then heated on the water bath. 1-Phenyl-1-(4-nitrophenyl)-ethane (I) was obtained in a yield of 65% of the theoretical.

The results of the nitration of 1,1-diphenylethane under different conditions are presented in the following scheme:



EXPERIMENTAL

1,1-Di-(4-nitrophenyl)-ethane (II). 5 g of 1,1-diphenylethane was introduced dropwise into 20 ml of HNO_3 (d 1.5) with constant shaking. The mixture was cooled to −15°. After addition of all of the diphenylethane, the mixture was poured onto ice at once. The viscous, resinous substance which separated was washed several times with hot and with cold water; after as complete a removal of water as possible, the mixture was triturated with ether. The crystals which separated were filtered off and the resinous residue was again triturated with ether. Such a treatment was repeated until separation of the crystals ceased. 5 g (66%) of 1,1-di-(4-nitrophenyl)-ethane (II) and 3 g of a resinous residue were obtained. After recrystallization from glacial acetic acid Substance (II) consisted of colorless crystals with a m.p. of 112° [4].

4 g (53%) of the same product was obtained by introduction of 5 g of 1,1-diphenylethane into a nitrating mixture of 12.6 ml of HNO_3 (d 1.35) and 19 ml of H_2SO_4 (d 1.84) at 30-35°.

8.03 mg sub.: 0.8232 ml N_2 (33°, 690 mm). 8.52 mg sub.: 0.8869 ml N_2 (33.5°, 688 mm). Found %: N 10.33, 10.46. $C_{14}H_{12}O_4N_2$. Calculated %: N 10.30.

The oxidation of Substance (II) by chromic anhydride gave 4,4'-dinitrobenzophenone with a m.p. of 188° [4].

2,4-Dinitrobenzophenone with a m.p. of 197° was obtained [11] by oxidation of 5 g of the resinous residue with 20 g of chromic anhydride in 120 ml of glacial acetic acid, after a 30-hour boiling of the mixture.

8.98 mg sub.: 0.7938 ml N_2 (20.8°, 718.7 mm). Found %: N 10.41. $C_{13}H_8O_5N_2$. Calculated %: N 10.3.

1,1-Di-(2,4-dinitrophenyl)-ethane (III). 5 g of 1,1-diphenylethane was added gradually at 30-35° to a mixture of 10 ml of HNO_3 (d 1.35) and 25 ml of H_2SO_4 (d 1.84). The light-yellow, resinous substance which formed was washed with soda and with water, and was then triturated with ether. 4.5 g of Substance (III) (45%) and 2 g of a resinous residue were obtained.

After recrystallization from glacial acetic acid, the 1,1-di-(2,4-dinitrophenyl)-ethane (III) consisted of greenish-yellow crystals with a m.p. of 157°.

9.14 mg sub.: 1.2838 ml N_2 (20.4°, 722 mm). 7.37 mg sub.: 1.1172 ml N_2 (20.5°, 715.9 mm). Found %: N 15.55, 15.36. $C_{14}H_{10}O_8N_4$. Calculated %: N 15.46.

2,4,2',4'-Tetranitrobenzophenone with a m.p. of 224° [11] was obtained by oxidation of Substance (III) by chromic anhydride.

1,1-Phenyl-(4-nitrophenyl)-ethane (I). 30 g of copper nitrate was added slowly at 30-35° to a solution of 30 g of 1,1-diphenylethane in 30 ml of acetic anhydride; then the mixture was heated for 5 hours at 85°. The filtered solution was distilled first at ordinary pressure (water, acetic acid and acetic anhydride distilled), then in vacuo. On refractionation, Substance (I) with a b.p. of 180-181° at 7 mm was obtained. The yield was 20 g (65%).

9.22 mg sub.: 0.5488 ml N_2 (22°, 712.1 mm). Found %: N 6.45. $C_{14}H_{13}O_2N$. Calculated %: N 6.12.

2 g of Substance (I) was oxidized by 8 g of CrO_3 in 40 ml of glacial acetic acid by a 7-hour boiling. 1.8 g of 4-nitrobenzophenone with a m.p. of 138° [14] separated.

8.43 mg sub.: 0.4831 ml N_2 (24.8°, 714.3 mm). Found %: N 6.16. $C_{13}H_9O_3N$. Calculated %: N 6.12.

The phenylhydrazone of 4-nitrobenzophenone with a m.p. of 142° [14] was obtained.

1,1-Diphenyl-2,2-dinitroethylene (VI). A mixture of 5 g of 1,1-diphenylethane was heated with 15 ml of HNO_3 (d 1.42) for 6 hours at 70-80° (water bath). A liberation of brown oxides of nitrogen was observed, and the mixture darkened. On pouring it into water, crystals which were impregnated with an oil separated. A total of 4 g (53%) of Substance (VI) and 3 g of oil were obtained.

Substance (VI), recrystallized from acetic acid, consisted of bright-yellow needles with a m.p. of 148°.

8.31 mg sub.: 0.7938 ml N_2 (22°, 715.1 mm). 8.36 mg sub.: 0.8330 ml N_2 (23°, 711.2 mm). Found %: N 10.40, 10.75. $C_{14}H_{10}O_4N_2$. Calculated %: N 10.37.

1,1-Diphenyl-1-hydroxy-2-nitroethane (IV). 5 g of 1,1-diphenylethane was heated with 15 ml of HNO_3 (d 1.21) for 7 hours on the boiling water bath. The treatment was as usual.

3.5 g (50%) of Substance (IV) and 3 g of resinous residue were obtained.

After recrystallization from glacial acetic acid, the 1,1-diphenyl-1-hydroxy-2-nitroethane (IV) consisted of lustrous, snow-white crystals with a m.p. of 108° [7].

From the resinous residue, benzophenone with a m.p. of 46° and an oxime of m.p. 144°, separated.

5.16 mg sub.: 0.2989 ml N_2 (26.6°, 718.2 mm). 5.86 mg sub.: 0.3331 ml N_2 (30.8°, 717.8 mm). Found %: N 6.05, 5.81. $C_{14}H_{13}O_3N$. Calculated %: N 5.76.

Yellow crystals with a m.p. of 88° (V) were obtained by boiling 5 g of Substance (IV) with 10 g of acetyl chloride for 2 hours. The yield was 1.3 g.

8.14 mg sub.: 0.4508 ml N_2 (19°, 718.5 mm). 7.47 mg sub.: 0.4086 ml N_2 (19°, 722 mm). Found %: N 6.12, 6.08. $C_{14}H_{11}O_2N$. Calculated %: N 6.22.

SUMMARY

1. The nitration of 1,1-diphenylethane under different conditions was studied.

2. The feasibility of production of the following substances was shown: di-(4-nitrophenyl)-ethane (66%), di-(2,4-dinitrophenyl)-ethane (53%), phenyl-(4-nitrophenyl)-ethane (65%), diphenyldinitroethylene (80%), diphenylhydroxynitroethane (53%), and diphenylnitroethylene.

3. It was observed that on heating 1,1-diphenylethane with concentrated nitric acid, nitration of the side chain resulted.

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* T. p. = C. B. Translation pagination.

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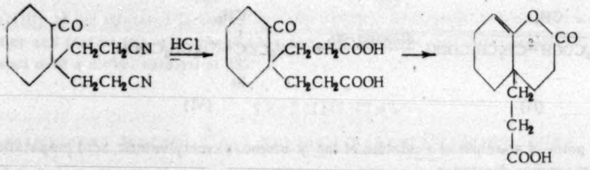
CYANOETHYLATED KETONES IN THE SYNTHESIS OF UNSATURATED δ-LACTONES

II. SYNTHESIS AND PROPERTIES OF THE UNSATURATED δ-LACTONE FROM γ-ACETYLVALERONITRILE

R. Ya. Levina, N. P. Shusherina and M. Yu. Lurye

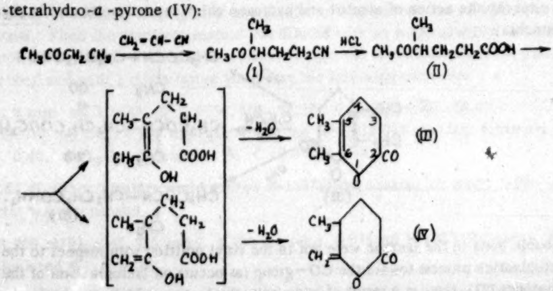
In connection with the presence of unsaturated lactone rings in the molecules of many antibiotics [1], a large number of investigations devoted to the study of the properties of the unsaturated γ-lactones have appeared recently [2]; at the same time, the unsaturated δ-lactones seem to be an almost uninvestigated class of compounds.

Earlier [3] a new method of synthesis of the unsaturated δ-lactones was described, wherein readily available cyanoethylated ketones were used as the starting materials, which were converted to the δ-ketonic acids by hydrolysis, and the unsaturated δ-lactones were formed from the acids by dehydration. The synthesis of the unsaturated δ-lactonic acid from dicyanoethylated cyclohexanone is the chief example of this reaction: *



The presence of the lactonic ring was demonstrated by opening it with an aqueous alkali solution, and also by alcohol in the presence of hydrogen chloride. The unsaturated nature of the resulting lactonic acid was confirmed by the usual reactions for the double bond.

In the present work, the unsaturated δ-lactone from γ-acetylvaleric acid (II), obtained by the hydrolysis of monocyanoethylated methyl ethyl ketone (I), was synthesized by this method (with a yield of 75-85% of the theoretical). On lactonization of γ-acetylvaleric acid, the formation of two unsaturated δ-lactones, differing by the position of the double bond (in the ring and outside of it) is possible – 5,6-dimethyl-3,4-dihydro-α-pyrone (III) and 5-methyl-6-methylene-tetrahydro-α-pyrone (IV):



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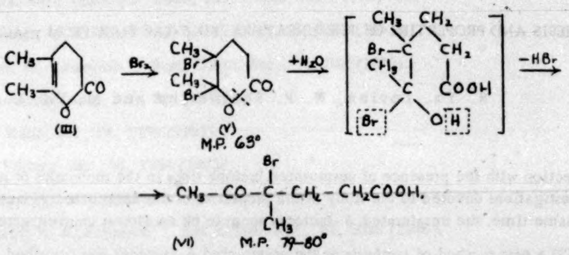
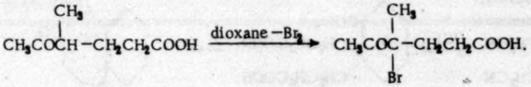
* It is interesting to note that Campbell and coworkers [4], attempting to reduce the ketonic group of a δ-ketonic acid (γ-acetyl-γ-phenylcaproic) by hydriodic acid (KI + H_3PO_4) and red phosphorus, obtained a substance which had a double bond, and which on analysis corresponded to the unsaturated lactone. However, since the substance displayed acid properties, liberating CO_2 from an aqueous soda solution, the authors decided not to ascribe to it the unsaturated δ-lactone structure.

We were able to determine the position of the double bond in the resulting lactone by means of the bromination reaction. The bromination product was the crystalline dibromide (V) with a melting point of 63°, which fumed very violently in the air, and after treatment with water was converted to γ-bromo-γ-acetylvaleric acid (VI) with a melting point of 79-80°.

Such a conversion may be represented by the following scheme:



For the identification of the γ-bromo-γ-acetylvaleric acid (VI) which formed, we obtained it by an alternate method — by the bromination of γ-acetylvaleric acid (II) by means of dioxanedibromide. *



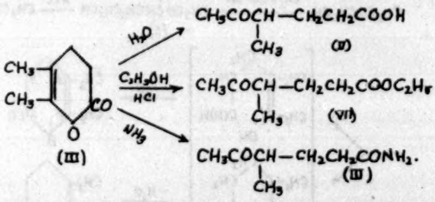
$$CH_3CO\overset{CH_3}{C}H-CH_2CH_2COOH \xrightarrow{\text{dioxane}-Br_2} CH_3CO\overset{CH_3}{\underset{Br}{C}}-CH_2CH_2COOH.$$

(II) (VI)

The melting point of a sample of a mixture of the γ-bromo-γ-acetylvaleric acid preparations obtained by these two methods showed no depression.

The unusual behavior of the dibromolactone, hydrolyzing unusually easily (under the action of water and even of the moisture of the air) with the splitting off of hydrogen bromide, and its conversion to γ-bromo-γ-acetylvaleric acid, was a definite demonstration that the double bond in the resulting unsaturated lactone is located in the ring, in the vinyl position with respect to oxygen, i.e., that the lactone is 5,6-dimethyl-3,4-dihydro-α-pyrone (III).

The structure of the resulting unsaturated lactone was confirmed also by the ready opening of the lactone ring, with conversion to the original ketonic acid, γ-acetylvaleric (by the action of a dilute aqueous solution of alkali), to its ester (by the action of alcohol and hydrogen chloride), and to its amide (by the action of an aqueous solution of ammonia):



If the double bond in the lactone were not in the vinyl position with respect to the oxygen, but was displaced during the lactonization process toward the CO— group (as occurs on lactonization of the γ-ketonic acids to unsaturated γ-lactones [2]), then as a result of hydrolysis the lactone which we obtained would be converted, not to the original saturated ketonic acid (II), but to the unsaturated hydroxy acid or, after the splitting off of water, to the di-unsaturated acid:

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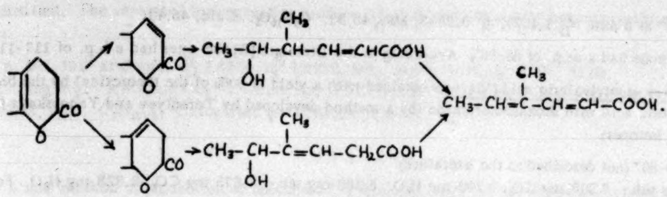
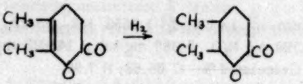
* As is known, the bromination of ketones proceeds with the replacement of the α-hydrogen at the least hydrogenated carbon atom [5].



Thus, it can be considered as demonstrated that no displacement of the double bond toward the CO−group takes place during the process of conversion of the δ-ketonic acid to the unsaturated δ-lactone.

The catalytic hydrogenation of the unsaturated δ-lactone over nickel on aluminum oxide at 200°, led to the production of the saturated lactone, 5,6-dimethyltetrahydro-α-pyrone (IX):



(VIII) (IX)

The stability of the saturated lactonic ring under catalytic hydrogenation conditions was observed also in the work of Sabatier and Mailhe [6], who obtained the pentanolide-1,4 (α-methylbutyrolactone) by the hydrogenation of levulinic acid over a nickel catalyst at 250°.

EXPERIMENTAL

Monocyanoethylated Methyl Ethyl Ketone (γ-Acetylvaleronitrile)

405 g (5.5 moles) of methyl ethyl ketone and 1 g of a 30% methanol solution of potassium hydroxide were placed in a flask equipped with a stirrer, reflux condenser, dropping funnel and thermometer; on cooling to 3-5° and with vigorous stirring, 30 g (0.54 mole) of acrylonitrile was added at such a rate that the temperature of the reaction mixture did not rise above 10°. Stirring was continued further for about 1 hour; the methyl ethyl ketone which did not react was removed, and the residue was vacuum distilled. 15-20 g (22-30%) of γ-acetylvaleronitrile (I) with a b.p. of 110-112° at 10 mm, and 25 g (50%) of γ-acetyl-γ-methylpimelonitrile with a m.p. of 67° (after recrystallization from benzene), were obtained.

The literature values for γ-acetylvaleronitrile [7]: b.p. 114-115° at 15 mm.

γ-Acetylvaleric acid. A mixture of 30 g of γ-acetylvaleronitrile and 180 ml of dilute (2 : 1) hydrochloric acid was boiled for 3 hours. Then the reaction mixture was diluted with an equal quantity of water and extracted with ether in an extractor for 10 hours. The ether was removed, and the residue was vacuum distilled. The γ-acetylvaleric acid (II), obtained with a quantitative yield, had the following constants:

B. p. 140-141° at 5 mm, n_D^{20} 1.4483, d_4^{20} 1.0674, MR_D 36.12. $C_7H_{12}O_3$. Calc. 36.07.

6.757 mg sub.: 14.072 mg CO_2; 4.980 mg H_2O. 6.430 mg sub.: 13.749 mg CO_2; 4.840 mg H_2O. Found %: C 58.40, 58.34; H 8.48, 8.42. $C_7H_{12}O_3$. Calculated %: C 58.29; H 8.46.

The semicarbazone of γ-acetylvaleric acid melted at 135° (from aqueous alcohol). After three recrystallizations its melting point was unchanged.

5.312 mg sub.: 0.969 ml N_2 (24°, 750 mm). 4.780 mg sub.: 0.878 ml N_2 (22°, 750 mm). Found %: N 20.69, 20.76. $C_8H_{15}O_3N_3$. Calculated %: N 20.89.

According to the literature [7], γ-acetylvaleric acid boils at 160-162° at 16 mm, and its semicarbazone melts at 160-161°.

The ethyl ester of γ-acetylvaleric acid (VII) was obtained (with a 75% yield) by boiling a solution of the acid (10 g) in anhydrous ethyl alcohol (35 ml) in the presence of concentrated sulfuric acid (1 g).

B. p. 95° at 5 mm, n_D^{20} 1.4320, d_4^{20} 0.9803, MR$_D$ 45.51. $C_9H_{16}O_3$. Calc. 45.43.

The semicarbazone had a m.p. of 95-96°. According to the literature [8] the ester had a b.p. of 117-118° at 23 mm.

γ-Bromo-γ-acetylvaleric acid (VI) was obtained with a yield of 90% of the theoretical by the bromination of γ-acetylvaleric acid with dioxanedibromide (by a method developed by Terentyev and Yanovskaya [9] for the bromination of ketones).

M. p. 79-80° (not described in the literature).

5.200 mg sub.: 7.205 mg CO_2; 2.282 mg H_2O. 6.298 mg sub.: 8.675 mg CO_2; 2.828 mg H_2O. Found %: C 37.81, 37.59; H 4.91, 5.02. $C_7H_{11}O_3Br$. Calculated %: C 37.69; H 4.97.

The Unsaturated δ-Lactone from γ-Acetylvaleric Acid (5,6-Dimethyl-3,4-dihydro-α-pyrone; 4-Methylhexenen-4-olide-1,5)

24 g of γ-acetylvaleric acid and 125 ml of acetic anhydride were boiled with several drops of acetyl chloride for 2 hours. The acetic anhydride was removed; the residue was washed several times with small portions of water, dried with magnesium sulfate and vacuum distilled. 18 g (85%) of the unsaturated δ-lactone (III) was obtained, which was a colorless, mobile liquid with a characteristic odor, and which readily decolorized an aqueous solution of permanganate and a solution of bromine in carbon tetrachloride. The lactone had the following constants:

B. p. 210° at 745 mm, 90° at 6-7 mm, n_D^{20} 1.4738, d_4^{20} 1.0552, MR$_D$ 33.62. $C_7H_{10}O_2$. Calc. 33.51.

4.620 mg sub.: 11.290 mg CO_2; 3.390 mg H_2O. 5.987 mg sub.: 14.625 mg CO_2; 4.350 mg H_2O. Found %: C 66.69, 66.66; H 8.12, 8.13. $C_7H_{10}O_2$. Calculated %: C 66.68; H 7.99.

The freshly-distilled lactone displayed no acid properties; on standing, it was partially hydrolyzed by the moisture of the air, being converted to the original ketonic acid.

The resulting unsaturated δ-lactone (5,6-dimethyl-3,4-dihydro-α-pyrone) was not described in the literature.

Bromination of the unsaturated δ-lactone. To a solution of 2 g of the unsaturated lactone in 2 ml of carbon tetrachloride, a solution of 2.5 g of bromine in the same solvent was added, with cooling. The solvent was distilled off in vacuo; the crystalline dibromide (V), after recrystallization from petroleum ether, melted at 63°. The dibromide fumed very violently in the air; after its treatment with water at room temperature a substance with a m.p. of 79-80° (from petroleum ether) was obtained, which contained bromine (Beilstein test) and had acid properties. According to analytical data and according to its melting point, the resulting substance corresponded to γ-bromo-γ-acetylvaleric acid (VI); the melting point of a sample of a mixture with known γ-bromo-γ-acetylvaleric acid (see above) showed no depression. The yield of the bromoketonic acid amounted to 2.8 g (80%).

Hydrolysis of the unsaturated δ-lactone. The lactone (III) was gradually converted to the original γ-acetylvaleric acid by the action of the moisture of the air. Titration by alkali of the lactone which had stood for several days after production showed the presence of appreciable quantities of acid in it. On standing with water for 4 days (at room temperature), the lactone was hydrolyzed by 40-50%. On heating the lactone with a 10% aqueous solution of potassium hydroxide for 1 hour there was a quantitative conversion of it to the ketonic acid, which was identified by its semicarbazone (m.p. 135°).

Ammonolysis of the unsaturated δ-lactone was carried out by shaking it in a funnel with a twofold quantity of concentrated aqueous ammonia. The resulting amide of acetylvaleric acid (not described in the literature) melted at 124° after recrystallization from ethyl acetate.

4.782 mg sub.: 0.424 ml N_2 (20°, 743 mm). 4.666 mg sub.: 0.416 ml N_2 (20°, 743 mm). Found %: N 10.10, 10.16. $C_7H_{13}O_2N$. Calculated %: N 9.77.

Alcoholysis of the unsaturated δ-lactone. A solution of 10 g of the lactone in 75 ml of anhydrous alcohol was saturated with hydrogen chloride, with cooling with ice for 2 hours. The reaction mixture was poured into 150 ml of water and extracted with ether. After the usual treatment, 8 g (66%) of the ester of γ-acetylvaleric acid was separated:

B. p. 95° at 5 mm, n_D^{20} 1.4300; its semicarbazone melted at 96-97°.

A sample of a mixture of the two semicarbazone preparations showed no depression on melting.

A catalytic hydrogenation of the unsaturated δ-lactone (20 g) was carried out over nickel on aluminum oxide at 200°. The catalyzate was washed with soda and with water, dried with calcined magnesium sulfate and vacuum distilled. The separated hydrogenation product (13 g) did not decolorize bromine water and had no acid properties.

B. p. 107-109° at 8 mm, n_D^{20} 1.4550, d_4^{20} 1.0222, MR_D 34.03. $C_7H_{12}O_2$. Calc. 33.98.

4.100 mg sub.: 9.820 mg CO_2; 3.480 mg H_2O; 4.725 mg sub.: 11.305 mg CO_2; 4.020 mg H_2O. Found %: C 65.36, 65.30; H 9.52, 9.28. $C_7H_{12}O_2$. Calculated %: C 65.59; H 9.42.

SUMMARY

1. A new method of production of unsaturated δ-lactones, with the use of cyanoethylated ketones as the starting materials, was developed.

2. The cyanoethylation of methyl ethyl ketone, hydrolysis of the γ-acetylvaleronitrile which formed to γ-acetylvaleric acid, and lactonization of the latter led to the production (75-85% yield) of the unsaturated δ-lactone, 5,6-dimethyl-3,4-dihydro-α-pyrone (not described in the literature).

3. The structure of the resulting unsaturated δ-lactone (presence of lactone ring) was demonstrated by the opening of the lactone ring, with conversion to the original ketonic acid (hydrolysis) to its ester (alcoholysis) and to the amide (ammonolysis).

4. By bromination of the resulting unsaturated δ-lactone, it was demonstrated that the double bond in it occurred in the ring, in the vinyl position with respect to the oxygen, i.e., that it was 5,6-dimethyl-3,4-dihydro-α-pyrone.

5. By hydrogenation of 5,6-dimethyl-3,4-dihydro-α-pyrone over nickel on aluminum oxide at 200°, the saturated δ-lactone, 5,6-dimethyltetrahydro-α-pyrone (not described in the literature) was obtained.

6. Several new derivatives of γ-acetylvaleric acid were obtained.

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Moscow State University

vacuum distilled. The separated hydrogenation product [illegible] in water, and had no acid properties.

B. p. 107-108° at 8 mm; [illegible]. Found %: [illegible]. Calculated %: [illegible].

SUMMARY

1. A new method of production of unsaturated δ-lactones, with the use of [illegible] as the starting materials, was developed.

2. The [illegible] of [illegible] vinyl [illegible] acid, and [illegible] of the latter led to the formation of [illegible] (first described in the literature).

3. The structure of the resulting unsaturated δ-lactone [illegible] of the lactone ring, with conversion to the [illegible].

4. By hydrogenation of the resulting unsaturated δ-lactone it was demonstrated that the double bond in it occurs in the ring, in the [illegible] position with respect to the carbonyl group, which was [illegible].

5. By hydrogenation of [illegible] lactone [illegible].

6. Several new derivatives of γ-acetylbutyric acid were obtained.

LITERATURE CITED

[1] [illegible]

[2] [illegible] J. Am. Chem. Soc. [illegible]; [illegible] J. Org. Chem. [illegible]

[3] [illegible]

[4] A. Campbell, [illegible], J. Chem. Soc., 1948, [illegible].

[5] [illegible] J. Am. Chem. Soc. [illegible]

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[8] [illegible] Ann. chim. [illegible]

[9] [illegible]

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[illegible] State University

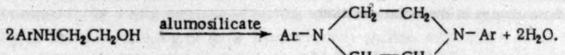
DEHYDRATION OF N-(β-HYDROXYETHYL)-ARYLAMINES IN THE PRESENCE OF ALUMOSILICATE

Yu. K. Yuryev and L. F. Gorin

The dehydration of N-(β-hydroxyethyl)-arylamines, with the formation of the corresponding N,N'-diarylpiperazines, has been studied only in the instances of N-(β-hydroxyethyl)-aniline and N-(β-hydroxyethyl)-p-toluidine. In the case of N-(β-hydroxyethyl)-p-toluidine the closing of the piperazine ring took place readily with ordinary boiling [1], whereas N-(β-hydroxyethyl)-aniline was not changed by heating with anhydrous oxalic acid [2], and N,N'-diphenylpiperazine was formed only by the action of phosphorus pentoxide in boiling xylol [3] or by heating with a copper-chromium catalyst at 250° under a hydrogen pressure of 250 atm [4].

Later one of us [5] showed that N,N'-diphenylpiperazine was formed readily by heating N-(β-hydroxyethyl)-aniline with alumo-silicate at 240°.**

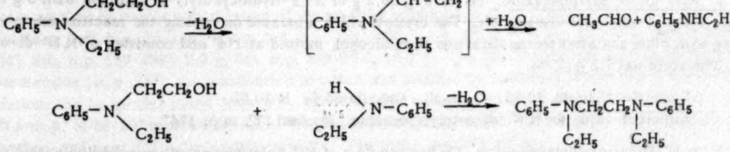
In the present work we carried out the dehydration of different N-(β-hydroxyethyl)-arylamines under the action of alumosilicate, and obtained the corresponding symmetrical N,N'-diarylpiperazines


2ArNHCH₂CH₂OH
alumosilicate
Ar–N
CH₂—CH₂
CH₂—CH₂
N–Ar + 2H₂O.

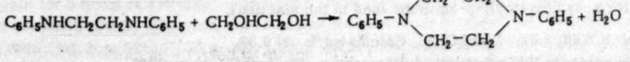
By the joint dehydration of N-(β-hydroxyethyl)-aniline, and also of N-(β-hydroxyethyl)-p-toluidine with aniline and with p-toluidine in the presence of alumosilicate, we obtained N,N'-diphenylethylenediamine and N'-N-phenyl-N'-p-tolylethylenediamine, respectively

$$RC_6H_4NHCH_2CH_2OH + H_2NC_6H_4R \rightarrow RC_6H_4NHCH_2CH_2NHC_6H_4R + H_2O.$$
$$(R = H,\ CH_3).$$

The heating of N-(β-hydroxyethyl)-N-ethylaniline with alumosilicate at 250-260° led to the production of N,N'-diethyl-N,N'-diphenylethylenediamine, apparently, via the stage of formation of N-vinyl-N-ethylaniline, the hydrolysis of the latter [6], and the joint dehydration of the original N-(β-hydroxyethyl)-N-ethylaniline with the N-ethylaniline which formed


C₆H₅–N
CH₂CH₂OH
C₂H₅
–H₂O
C₆H₅–N
CH=CH₂
C₂H₅
+H₂O
CH₃CHO+C₆H₅NHC₂H₅
C₆H₅–N
CH₂CH₂OH
C₂H₅
+
H
N–C₆H₅
C₂H₅
–H₂O
C₆H₅–NCH₂CH₂N–C₆H₅
C₂H₅
C₂H₅

Finally, N,N'-diphenylpiperazine was obtained by means of the joint dehydration of N,N'-diphenylethylenediamine with ethylene glycol under the same conditions


C₆H₅NHCH₂CH₂NHC₆H₅ + CH₂OHCH₂OH
C₆H₅–N
CH₂–CH₂
CH₂–CH₂
N–C₆H₅ + H₂O

The diarylpiperazines and diarylethylenediamines, obtained in the present work, are cited in the Table.

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* We obtained N,N'-diphenylpiperazine with a yield of 54%.

Initial Substance	Reaction products	Melting point	Yield (in % of the theoretical)
N-(β-hydroxyethyl)-aniline	N,N'-diphenylpiperazine	163*	54
N,N'-diphenylethylenediamine + ethylene glycol	N,N'-diphenylpiperazine	163	90
N-(β-hydroxyethyl)-p-toluidine	N,N'-di-p-tolylpiperazine	189	95
N-(β-hydroxyethyl)-o-toluidine	N,N'-di-o-tolylpiperazine	174	27
N-(β-hydroxyethyl)-p-anisidine	N,N'-di-p-anisidylpiperazine	233	50
N-(β-hydroxyethyl)-o-anisidine	N,N'-di-o-anisidylpiperazine	139	10
N-(β-hydroxyethyl)-o-chloroaniline	N,N'-di-o-chlorophenylpiperazine	180	16.5
N-(β-hydroxyethyl)-α-naphthylamine	N,N'-di-α-naphthylpiperazine	265	15
N-(β-hydroxyethyl)-aniline + aniline	N,N'-diphenylethylenediamine	65	40
N-(β-hydroxyethyl)-aniline + p-toluidine	N-phenyl-N'-p-tolylethylenediamine	59	80
N-(β-hydroxyethyl)-p-toluidine + aniline	N-phenyl-N'-p-tolylethylenediamine	59	67.5
N-(β-hydroxyethyl)-N-ethylaniline	N,N'-diethyl-N,N'-diphenylethylenediamine	71	63

It is evident from the data of the Table that the presence of methyl or methoxyl in the para-position – both in N-(β-hydroxyethyl)-arylamine, and in arylamine – conditions the production of a higher yield of N,N'-diarylpiperazine and, consequently, of N,N'-diarylethylenediamine. The yields of the reaction products decreased sharply with the presence of these groups in the ortho-position.

EXPERIMENTAL

Production of N,N'-Diarylpiperazines from N-(β-Hydroxyethyl)-arylamines

1. N,N'-Di-p-tolylpiperazine. 15.0 g of N-(β-hydroxyethyl)-p-toluidine and 3 g of alumosilicate cracking catalyst were heated for 5 hours in a small retort at 230-240° in a nitrogen atmosphere. 1.8 g of water was distilled off. After cooling, the reaction substance was completely crystallized. The crude reaction product melted at 177°; after washing with ether and after recrystallization from alcohol the substance melted at 189° and consisted of N,N'-di-p-tolypiperazine. The yield was 12.6 g (95%).

Found %: N 10.46, 10.50. $C_{18}H_{22}N_2$. Calculated %: N 10.52.
Literature data for N,N'-di-p-tolylpiperazine: Demole [1], m.p. 189–190°, Bischoff [7], m.p. 187°.

2. N,N'-Di-o-tolylpiperazine. On heating 30.2 g of N-(β-hydroxyethyl)-o-toluidine with 6 g of alumosilicate, 3.2 g of water was distilled off. The crystals which separated on cooling the reaction substance, after washing with ether and after recrystallization from alcohol, melted at 174° and consisted of N,N'-di-o-tolylpiperazine. The yield was 7.5 g (27%).

Found %: N 10.42, 10.70. $C_{18}H_{22}N_2$. Calculated %: N 10.52.
Literature value for N,N'-di-o-tolypiperazine: Bischoff [7], m.p. 174°.

3. N,N'-Di-p-anisidylpiperazine. On heating 20 g of N-(β-hydroxyethyl)-p-anisidine with 4 g of alumosilicate, 0.4 g of water was distilled. After vacuum distillation of the unchanged N-(β-hydroxyethyl)-p-anisidine (13.5 g), the residue crystallized. After washing with a mixture of chloroform and alcohol and recrystallization from pyridine, the crystals melted at 233° and consisted of N,N'-di-p-anisidylpiperazine. The yield was 3 g [50% on the basis of the N-(β-hydroxyethyl)-p-anisidine used in the reaction].

Found %: N 9.66, 9.62. $C_{18}H_{22}O_2N_2$. Calculated %: N 9.39.
Literature value for N,N'-di-p-anisidylpiperazine: Bischoff [7], m.p. 233°.

4. N,N'-Di-o-anisidylpiperazine. On heating 20 g of N-(β-hydroxyethyl)-o-anisidine with 4 g of alumosilicate, 0.2 g of water was distilled. The crystals which separated on cooling, were filtered and washed with a mixture of chloroform and alcohol. After recrystallization from pyridine they melted at 139° and consisted of N,N'-di-o-anisidylpiperazine. The yield was 1.8 g (10%).

Found %: N 9.65, 9.42. $C_{18}H_{22}O_2N_2$. Calculated % : N 9.39.

N,N'-Di-o-anisidylpiperazine was difficulty soluble in alcohol, chloroform and benzene, and more readily soluble in ether; it was not described in the literature.

5. N,N'-Di-o-chlorophenylpiperazine. From 10 g of N-(β-hydroxyethyl)-o-chloroaniline, heated with 2 g of alumosilicate, as described above, N,N'-di-o-chlorophenylpiperazine was obtained, which after washing with ether and after recrystallization from anhydrous alcohol melted at 180°. The yield was 1.5 g (16.5%). The N,N'-Di-o-chlorophenylpiperazine was highly soluble in chloroform, and less soluble in ether and in alcohol; it was not described in the literature.

Found %: N 9.52, 9.46. $C_{16}H_{16}N_2Cl_2$. Calculated %: N 9.82.

6. N,N'-Di-α-naphthylpiperazine. 10.2 g of N-(β-hydroxyethyl)-α-naphthylamine was heated with 2 g of alumosilicate. The unreacted N-(β-hydroxyethyl)-α-naphthylamine (6 g) was vacuum distilled. On addition of alcohol to the residue N,N'-di-α-naphthylpiperazine crystallized out, which was filtered off, washed with a mixture of ether and alcohol, and after recrystallization from pyridine, melted at 265°. The yield was 0.6 g [15% of the theoretical, on the basis of the N-(β-hydroxyethyl)-α-naphthylamine used].

Found %: N 8.47, 8.47. $C_{24}H_{22}N_2$. Calculated %: N 8.28.
Literature value for N,N'-di-α-naphthylpiperazine: Bischoff [7], m.p. 265°.

Production of N,N'-Diarylethylenediamines

1. N,N'-Diphenylethylenediamine. 13.7 g (0.1 mole) of N-(β-hydroxyethyl)-aniline and 58.5 g (0.6 mole) of aniline were heated for 5 hours at 230-240° with 14.5 g of alumosilicate in a flask with a fractionating column and a reflux condenser. 18 g of a mixture of aniline and water was distilled. After removal of the alumosilicate by filtration, 42 g of aniline and 0.5 g of N-(β-hydroxyethyl)-aniline were driven off by vacuum distillation. From the residue, by the addition of 80% alcohol, 2.5 g (21.7%) of N,N'-diphenylpiperazine with a m.p. of 153° was crystallized, which after recrystallization from 80% alcohol melted at 163°; a sample of a mixture with known N,N'-diphenylpiperazine disclosed no depression.

N,N'-Diphenylethylenediamine, melting at 65° after repeated recrystallization from alcohol, separated from the filtrate on dilution with water. The yield was 8.5 g (40%). A sample of a mixture with known N,N'-diphenylethylenediamine disclosed no depression.

Found %: N 13.03, 13.19. $C_{14}H_{16}N_2$. Calculated %: N 13.08.
Literature data for N,N'-diphenylethylenediamine: Bischoff [8], m.p. 65°.

2. N-Phenyl-N'-p-tolylethylenediamine. a) 13.7 g (0.1 mole) of N-(β-hydroxyethyl)-aniline and 64 g (0.6 mole) of p-toluidine were heated for 5 hours with 15 g of alumosilicate at 230-240°, as described above. 14 g of a mixture of p-toluidine and water was distilled off. After removal of the alumosilicate by filtration, the following fractions were separated by vacuum distillation of the reaction product at 4 mm: 1st, b.p. 55°, 40 g, with a m.p. of 45° (p-toluidine); 2nd, b.p. 55-138°, 1.2 g; 3rd, b.p. 138-139°, 1.1 g, n_D^{20} 1.5763 and d_4^{20} 1.0941 [N-(β-hydroxyethyl)-aniline]; 4th, b.p. 139-198°, 2.2 g; 5th, b.p. 198-200°, 18.3 g. The 5th fraction was crude N-phenyl-N'-p-tolylethylenediamine (m.p. 55°), the purification of which was attained by fractional precipitation with water from alcoholic solution; the impurities came down first, but on further dilution crystals of pure N-phenyl-N'-p-tolylethyenediamine with a m.p. of 58-59° separated, which were leaflets with a mother-of-pearl luster, readily soluble in alcohol and in ether, and very difficulty soluble in water. The yield was 18 g (80%).

Found %: N 12.40, 12.38. $C_{15}H_{18}N_2$. Calculated %: N 12.27.

b) 15.1 g (0.1 mole) of N-(β-hydroxyethyl)-p-toluidine and 55 g (0.6 mole) of aniline were heated with 17 g of alumosilicate for 5 hours at 230-240° as described above. 24 g of aniline and water were distilled off. After removal of the alumosilicate by filtration, the following fractions were separated by vacuum distillation of the reaction product at 5 mm: 1st, b.p. 52-53°, 24 g, n_D^{20} 1.5841 and d_4^{20} 1.0223 (aniline); 2nd b.p. 53-146°, 1.2 g, n_D^{20} 1.5793; 3rd, b.p. 146-147°, 2.4 g with a m.p. of 42° [N-(β-hydroxyethyl)-p-toluidine]; 4th b.p. 147-199°, 1.5 g; 5th, b.p. 199-213°, m.p. 54°, 15.3 g – N-phenyl, N'-p-tolylethylenediamine.

By fractional precipitation of the alcoholic solution of the 5th fraction with water (as described above), 13 g 67.5% of N-phenyl, N'-p-tolylethylenediamine was separated, which after drying in vacuo and after recrystallization from alcohol melted at 59° and was identical with the N-phenyl-N'-p-tolylethylenediamine obtained in the previous experiment; a sample of a mixture disclosed no depression (m.p. 59°).

3. N,N'-Diethyl-N,N'-diphenylethylenediamine. 24 g (0.14 mole) of N-(β-hydroxyethyl)-N-ethylaniline and 5 g of alumosilicate were heated for 4 hours at 250-260°. The reaction product was fractionated in vacuo, whereby the following fractions were separated: 1st b.p. up to 190° (15 mm), 3 g; 2nd, b.p. 190-200° (2 mm), 16 g; residue, 3 g.

12 g (63%) of a substance going over at 194-196° (2 mm) and crystallizing on standing was obtained by redistillation of the 2nd fraction. The substance melted at 71° after recrystallization from alcohol and consisted of N,N'-diethyl-N,N'-diphenylethylenediamine.

Found %: N 10.56, 10.52. $C_{18}H_{24}N_2$. Calculated %: N 10.44.
Literature value for N,N'-diethyl-N,N'-diphenylethylenediamine: Hoffmann [9] m.p. 70°, Frohlich [10], m.p. 75°.

Production of N,N'-Diphenylpiperazine from N,N'-Diphenylethylenediamine and Ethylene Glycol

3 g of N,N'-diphenylethylenediamine and 0.6 g of ethylene glycol were heated with 0.7 g of alumosilicate, as described in experiment 1, 2 (b), for 6 hours at 230-240°. 2.9 g (90%) of N,N'-diphenylpiperazine with a m.p. of 163° was obtained after removal of the catalyst, washing with water and with ether, and after recrystallization from alcohol. A sample of a mixture with known N,N'-diphenylpiperazine disclosed no depression.

The picrate (from alcohol) consisted of yellow needles with a m.p. of 172-173°. A sample of a mixture with the known picrate of N,N'-diphenylpiperazine disclosed no depression.

Literature values for N,N'-diphenylpiperazine: Yuryev and Novitsky [5] – m.p. 163°, picrate m.p. 172-173°; Korshak and Strepikheev [11] – m.p. 163-164°, Pollard [4] – m.p. 163.5-164.5°; C. Bischoff [7] – m.p. 163°.

SUMMARY

1. The dehydration of N-(β-hydroxyethyl)-arylamines in the presence of alumosilicate at 230-240° led to the production of symmetrical N,N'-diarylpiperazines.

2. The joint dehydration of N-(β-hydroxyethyl)-arylamines with aromatic amines in the presence of alumosilicate led to N,N'-diarylethylenediamines and may serve as a method of production of both symmetrical and asymmetrical N,N'-diarylethylenediamines.

3. The heating of N-(β-hydroxyethyl)-N-ethylaniline with alumosilicate at 250-260° led to N,N'-diethyl-N,N'-diphenylethylenediamine.

4. The joint dehydration of N,N'-diphenylethylenediamine with ethylene glycol in the presence of alumosilicate led to the production of N,N'-diphenylpiperazine and may serve as a method of production of asymmetrical N,N'-diarylpiperazines.

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PRODUCTION OF β-n-AMYL- AND β-PHENYLTHIOPHANE BY CATALYTIC CONVERSION OF THE CORRESPONDING FURANIDINES

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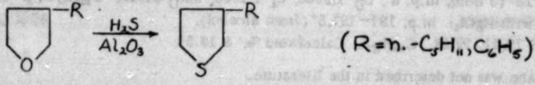
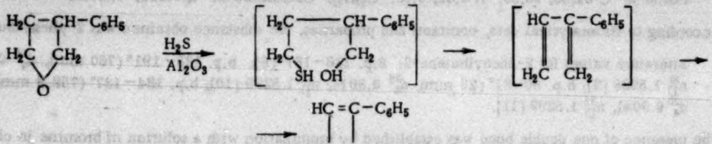
In the catalytic conversion of oxygen-containing heterocycles to cycles with other hetero-atoms, described and studied by one of us, both α-alkyl- [1] and β-alkylfuranidines [2], and also dialkylfuranidines of different structure [3], were included. By the action of hydrogen sulfide on them in the presence of aluminum oxide at an elevated temperature they all were converted with high yields to their corresponding thiophanes. β-Methyl-, β-ethyl-, β-propyl-, and β-butylthiophanes were obtained by such a method from the β-alkylfuranidines with yields of 72-81% [2], by which it was found that an increase of the number of carbon atoms in the side chain of the β-alkylfuranidines is related to the yield of the thiophane homologs to a lesser degree than in the conversion of the α-alkylfuranidines.

In the present work the effect on the conversion process of further complication of the alkyl in the initial β-alkylfuranidine, and also the effect on the conversion process of the phenyl radical in β-phenylfuranidine, were studied. β-Amylthiophane, with a yield of 64%, was obtained by passing β-n-amylfuranidine over aluminum oxide in a current of hydrogen sulfide. Under the same conditions β-phenylfuranidine gave β-phenylthiophane with a yield of 58%.



A by-product of the transformation of β-phenylfuranidine was 2-phenylbutene-2, the formation of which may be represented as a result of the opening of the oxide ring under the action of hydrogen sulfide, with the formation of 1-hydroxy-2-phenylbutane-4-thiol, followed by the splitting off of water and hydrogen sulfide from it, with the formation of 2-phenylbutadiene, and reduction of the latter with the addition of hydrogen in the 1,4-position.



In previous works on the conversion of α- and β-alkylfuranidines to the corresponding thiophanes no formation of reaction by-products was observed; therefore, it is certain that the possibility of the partial splitting off of water and hydrogen sulfide from the di-primary intermediate 1,4-mercapto compound was conditioned by the effect of the phenyl radical located on the β-carbon atom of the furanidine ring.

One of us observed the simultaneous splitting off of water and hydrogen sulfide with the formation of unsaturated hydrocarbons only for those γ-oxides which, by the action of hydrogen sulfide, probably in the intermediate stage, give a di-tertiary or, but to a lesser degree, primary-tertiary, 1,4-mercaptohydroxy compound, as occurred, for example, in the instance of the introduction of 2,2,5,5-tetramethylfuranidine [4] or, correspondingly, 2,2-dimethylfuranidine, into the reaction [5].

Thus, the secondary formation of 2-phenylbutene-2 serves as an additional confirmation of the validity of the proposal by one of us of a scheme for the mechanism of the catalytic conversion of oxygen-containing heterocycles to cycles with other hetero-atoms [6].

As to a further increase of the number of carbon atoms in the side chain of the β-alkylfuranidines, it should be noted that this again conditions a certain decrease of the corresponding thiophane homolog yield; according to the reaction described, β-n-butylthiophane was obtained with a yield of 79% [2], whereas in the present work β-n-amylthiophane was obtained with a yield of 64%.

EXPERIMENTAL

β-n-Amylfuranidine and β-phenylfuranidine were passed at a rate of 5-6 drops per minute into a strong current of hydrogen sulfide through a tube with an internal diameter of 10 mm, which was filled with aluminum oxide (length of catalyst layer 40 cm) and heated at about 350°. The receiving vessel was cooled with snow and salt. The catalyzate was extracted with ether. The ether extracts of the catalyzates were washed with an alkali solution and dried with fused potassium hydroxide. After driving off the ether the reaction product was vacuum distilled.

β-n-Amylthiophane. 4.25 g (64%) of β-n-amylthiophane was obtained from 6 g of β-n-amylfuranidine (b.p. 69-70° at 12 mm, n_D^{20} 1.4378, d_4^{20} 0.8602 [7]). This was a colorless liquid with a characteristic odor, soluble in ether, alcohol, and acetone, and having the following constants:

B.p. 92–93° (10 mm), n_D^{20} 1.4870, d_4^{20} 0.9151, MR_D 49.75. $C_9H_{18}S$. calc. 49.63.
Compound with $HgCl_2$ m.p. 89.5–90.5° (from alcohol). Found %: S 20.24, 20.35.
$C_9H_{18}S$. Calculated %: S 20.25.

β-n-Amylthiophane was not described in the literature.

β-Phenylthiophane. 4.3 g (58%) of β-phenylthiophane, having the following constants, was obtained from 6.7 g of β-phenylfuranidine (b.p. 81.5-82.5° at 4 mm, n_D^{20} 1.5442, d_4^{20} 1.0448) [7]:

B.p. 112–113° (5 mm), m.p. 6°, n_D^{20} 1.6000, d_4^{20} 1.1009, MR_D 51.10. $C_{10}H_{12}S \vDash_3$. calc. 50.65.
Compound with $HgCl_2$: m.p. 187–187.5° (from alcohol).
Found %: S 19.41, 19.38. $C_{10}H_{12}S$. Calculated %: S 19.51

β-Phenylthiophane was not described in the literature.

1.2 g of a considerably lower-boiling fraction, which decolorized bromine water and after redistillation had the following constants, was also separated on distillation of the reaction product:

B.p. 181–183° (742 mm), n_D^{20} 1.5300, d_4^{20} 0.9034, MR_D 44.28. $C_{10}H_{12} \vDash_4$. calc. 44.31.
Found %: C 91.06, 90.89; H 9.02, 9.08. $C_{10}H_{12}$. Calculated %: C 90.90; H 9.09.

According to its analytical data, constants and properties, the substance obtained was 2-phenylbutene-2.

Literature values for 2-phenylbutene-2: B.p. 186–187° [8]; b.p. 188–191° (760 mm), d_4^{22} 0.909, n_D^{22} 1.5288 [9]; b.p. 80–81° (20 mm), d_4^{25} 0.8911, n_D^{25} 1.5299 [10]; b.p. 184–187° (752.9 mm), d_4^{20} 0.9041, n_D^{21} 1.5299 [11].

The presence of one double bond was established by bromination with a solution of bromine in chloroform at −12°.

0.1902 g sub.: consumed for titration 0.224 g bromine; theoretically required quantity of bromine: 0.230 g.

Benzoic acid with a m.p. of 121° was obtained by oxidation with potassium permanganate in a neutral solution. A sample of a mixture with known benzoic acid displayed no melting point depression.

SUMMARY

1. β-n-Amylfuranidine and β-phenylfuranidine were converted to β-n-amylthiophane and β-phenylthiophane, respectively, under the conditions of catalytic conversion of oxygen-containing hetero-cycles to cycles with other hetero-atoms.

2. On conversion of β-phenylfuranidine to β-phenylthiophane, the formation of a by-product of the reaction, 2-phenylbutene-2, took place, which was conditioned by the effect of the phenyl radical bound to the β-carbon atom of the furanidine ring.

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* T.p. = C. B. Translation pagination.

THE MECHANISM OF HETEROGENEOUS CATALYTIC ISOMERIZATION OF HYDROCARBONS BY ACID CATALYSTS

II. MECHANISM OF FORMATION OF TERPINOLENE AND TERPINENES BY CATALYTIC ISOMERIZATION OF PINENE AND LIMONENE BY TITANIC ACID

G. A. Rudakov, M. M. Shestaeva, A. T. Marchevsky and Z. S. Khomenko

It was shown in a previous report [1] that limonene and camphene are rapidly isomerized and racemized by heating with titanic acid, and that at the same time, these terpenes, soluble in pinene, do not undergo changes on heating with the same catalyst in the presence of a sufficient concentration of pinene in solution.

This earlier, unknown characteristic of the isomerization transformations of terpenes enabled us to carry out a further investigation, interpreting the mechanism of isomerization of pinene to terpinolene, and also of pinene and limonene to α- and γ-terpinenes, on heating with titanic acid.

Besides camphene and limonene (II), terpinolene (III) is formed by the catalytic isomerization of pinene (I) on clays, titanic acid and other catalysts. Since, in its turn, limonene is readily isomerized to terpinolene, it was impossible until recently to answer with complete definiteness the question of whether terpinolene, obtained by the catalytic isomerization of pinene, was a product of the isomerization of both pinene and limonene, or was the product of the isomerization of only the latter. Considering the reaction from the point of view of ideas already stated [1, 2], it can be assumed that terpinolene should be obtained not only as a result of the isomerization of limonene, but also directly from pinene, since the conversion of pinene to limonene and to terpinolene must be brought about via the formation of the same intermediate compound or the ion (IV) corresponding to it.

We were able to solve the problem experimentally after it became known that the conversion of linonene to terpinolene by titanic acid did not take place in the presence of pinene, if the content of the latter in a solution of the isomerization products was above 25-30%. For this it was necessary to investigate the composition of the products of the incomplete isomerization of pinene, by stopping at the pinene content in the isomerizate, by eliminating the formation of terpinolene from limonene. The investigation showed the presence of terpinolene in the isomerizates containing unreacted pinene and, consequently, undoubtedly its primary origin. Since terpinolene and limonene formed from the same intermediate compound, the ratio between them remained constant until a sufficient quantity of pinene was present in the solution to render impossible the secondary reaction of the conversion of limonene to terpinolene. Only after the content of the unreacted pinene fell below a definite limit did the increase of the terpinolene content in the reaction products begin (see Table).

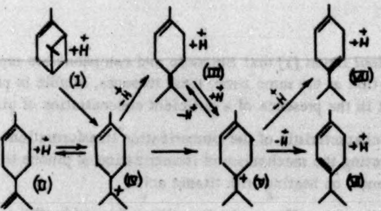
The resulting ratio between the quantities of limonene and terpinolene which formed during the initial period of the reaction, i.e., in the presence of above 25-30% of pinene in solution, enabled us to determine the approximate ratio of the rates of conversion of pinene to limonene and to terpinolene as 3 : 1.

As to the α- and β-terpinenes obtained by the acid isomerization of pinene and limonene, they are usually considered as secondary reaction products. It is assumed the terpinenes are formed from terpinolene, which is obtained from pinene and limonene at an early stage of the reaction. Such a view is probably based on the assumption that the reaction in the present case consists of a series of consecutive additions of acid to the double bond of the hydrocarbon and is the reverse of cleavages.

Considering the reaction as ionic, the terpinenes forming from pinene and limonene may be considered as not only secondary, but also as primary reaction products.

Composition of the Monocyclic Terpenes Obtained from Pinene by Catalytic Isomerization by Titanic Acid, in Relation to the Extent of Conversion

Experiment	Temperature of experiment	Charge of catalyst (in %)	Per cent of unreacted pinene	Composition of monocyclic terpenes (in %)		
				limonene	terpinolene	α-terpinene
1	135°	0.5	76	68	27	2.9
2	160	0.07	72	67	26	3.2
3	160	0.2	46	72	23	3.2
4	160	0.1	32	62	31	3.3
5	160	0.2	0	50	40	7.5



Gaining a proton from the catalyst, pinene and limonene are converted to the carbonium ion (IV). If titanic acid or a pinene-insoluble catalyst analogous to it is used as the catalyst, carbonium ion will exist only on the surface of the catalyst in the composition of a compound of the $\overset{+}{R}\overset{-}{X}$ [1] type, which does not prevent its undergoing all the rearrangements characteristic of carbonium ions [3-5]. The isomerization of part of the ions (IV) to ions (V) is most likely in the present case. The (V) ions, returning the proton to the catalyst, should be converted to terpinenes (VI) and (VII) or to terpinolene (III).

If the presence of a direct conversion of pinene or limonene to terpinenes without the formation of terpinolene as the necessary intermediate product should be demonstrated, then a serious basis for the use of the ionic mechanism of this reaction would be obtained.

After it became known that the isomerization conversion of limonene by titanic acid did not occur if α-pinene was present in sufficient concentration in the solution of terpenes reacting, there was assurance that terpinolene also close in structure to limonene, likewise would not isomerize in the presence of pinene. It was therefore possible, to a high degree of probability, to solve the problem of the presence of a direct conversion of pinene (and consequently, also limonene) to terpinenes by the presence of α- and γ-terpinenes, or even relatively easily by determining the α-terpinene in the monocyclic terpenes obtained by the incomplete isomerization of pinene. An investigation of these monocyclic terpenes not only established the presence of α-terpinene in them, but also showed that the ratio between the limonene, terpinolene and α-terpinene contained in the monocyclic terpenes was maintained constant until there was a sufficient quantity of pinene in the solution, and only with a decrease of the pinene concentration below 30% did the terpinolene and α-terpinene contents in the monocyclic terpenes begin to increase, and the limonene content to decrease (see Table). Such a course of the process definitely confirmed the primary origin of the α-terpinene at the initial stage of the reaction, which terminated at a sufficiently high pinene concentration in the solution. If at this stage of the reaction α-terpinene is not obtained directly from pinene, but from terpinolene, the α-terpinene content in the monocyclic terpenes would not be maintained constant, but would increase continuously, since the rate of formation of the terpinenes would increase with an increase of the terpinolene concentration in the solution. The increase of the α-terpinene content in the monocyclic terpenes after decrease of the pinene content in the solution below 30% indicates the beginning of the formation of α-terpinene from terpinolene.

The statement confirms the above-developed ionic scheme of the formation of terpinenes from pinene and limonene.

EXPERIMENTAL

Starting materials. The α-pinene used for the investigation was isolated from Pinus sylvestris turpentine. The physical properties of the α-pinene were: d_4^{20} 0.8582, n_D^{20} 1.4655, $[\alpha]_D$ + 29.6°.

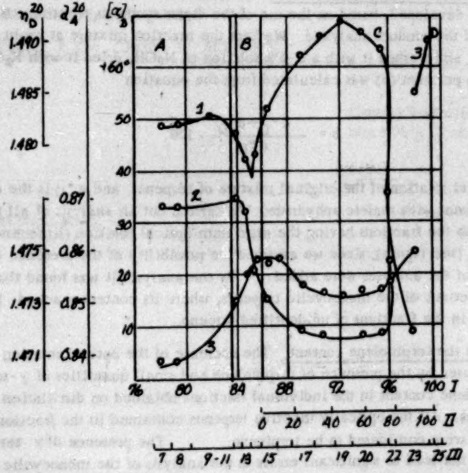
Titanic acid was used as the catalyst [1, 6]. The isomerization of pinene was carried out in the liquid phase with continuous stirring. In the production of an isomerizate containing no pinene, a careful control of the process was carried out in order to stop the reaction as soon as possible when all the pinene had reacted, since a longer heating of the isomerizate with the catalyst would lead to further change of its composition.

Analysis of the Isomerizates

Determination of the amounts of camphene, tricyclene and fenchenes. 1 g of the isomerizate was shaken for 10 minutes with 0.5-1 g (see content of substances determined) of an acid mixture consisting of 90% of 97% HCOOH and 10% of 96-100% H_2SO_4 [7]. 0.15-0.30 ml of water was added and the acids which separated from the solution were removed. After a second washing, the product was completely neutralized and dried with soda. We saponified a weighed portion (0.7-1 g) of the dried substance with a 0.15 N alcoholic solution of NaOH at room temperature for 20 minutes, after which we back-titrated the unreacted NaOH.

Determination of the content of monocyclic terpenes. The content of monocyclic terpenes in the isomerizates was found on the basis of data obtained by an analytic fractionation of the isomerizates with an apparatus of high efficiency.

The data obtained by distillation of one of the isomerizates investigated, which may be considered as typical, are cited in the figure.



Fractionation of an isomerizate containing 46% of unreacted pinene (see Table, Experiment 3).
I) Total distilled (in %); II) Monocyclic terpenes distilled (in %); III) Number of fractions.
1) $[\alpha]_D$, 2) d_4^{20}, 3) n_D^{20}.
A) Pinene and camphene (Fractions 9-11 had a m. p. of 39°); B) Unidentified terpene; C) Monocyclic terpenes; D) Residue from distillation.

Calculation of the pinene content. The pinene content in the isomerizates (B) was determined from the difference, B = 100 − A, where A is the sum of the camphene, tricyclene, fenchenes and monocyclic terpenes found, expressed in percentages.

Since on determination of camphene, pinene is converted by 10% into the ester, the results were divided by 0.90. The results of the camphene determination were corrected in a suitable way.

Determination of the limonene content. The monocyclic terpenes obtained by isomerization of pinene, contain only one optically active component — limonene; therefore, a calculation of the limonene content (b) in each fraction of monocyclic terpenes could be made by the formula

$$b = \frac{[\alpha']_D}{[\alpha'']_D} \cdot 100.$$

where $[\alpha']_D$ is the specific optical rotation of the fraction analyzed, and $[\alpha'']_D$ is the specific optical rotation of the limonene obtained from the original pinene. The results of the determinations of limonene in all the fractions were added up.

In the calculations for $[\alpha]_D$ of limonene we used the $[\alpha]_D$ of the strongest rotating fraction of monocyclic terpenes. The absence in these fractions of admixtures of the optically inactive terpinolene and terpinenes was confirmed by the fact that in the isomerizates which contained above 30% of unreacted pinene (see Table, Experiments 1-4), the strongest rotating fraction of monocyclic terpenes had a similar value $[\alpha]_D + 68.8 \pm 0.3°$, which agreed with the calculated $[\alpha]_D + 69.2°$.[*] According to its other properties (d_4^{20} 0.8419-0.8431, n_D^{20} 1.4730; tetrabromides: optically active forms with m.p. of 105° and racemic form with a m.p. of 125°) this fraction also corresponded to limonene. Limonene with $[\alpha]_D + 47°$ was isolated from the isomerizate which contained no pinene and differed from that described only in that it was partially racemized during the reaction.

Determination of the α-terpinene content. The quantitative determination of α-terpinene was carried out by a method which we developed, based on the use of the diene synthesis reaction. 0.5-1 g of maleic anhydride was added to 3-5 ml of the product analyzed. We kept the reaction mixture at room temperature for 3-5 days, stirring it periodically, and washed it with a 3-5% solution of NaOH, dried it with K_2CO_3 and determined α_D. The α-terpinene content in per cent (b) was calculated from the equation

$$b = \frac{\alpha''_D - \alpha'_D}{\alpha''_D} \cdot 100.$$

where α'_D is the optical rotation of the original mixture of terpenes, and α''_D is the optical rotation of the mixture of terpenes after treatment with maleic anhydride. We carried out an analysis of all the monocyclic terpene fractions withdrawn with the fractions having the maximum optical rotation (limonene), and also of some fractions of unidentified terpene (see figure), since we assumed the possibility of the presence of α-terpinene also in these fractions. The results of the analyses were added. By the analyses it was found that α-terpinene was concentrated in the initial fractions of the monocyclic terpenes, where its content reached 10-20%. Only 2-4% of α-terpinene was found in the fractions of unidentified terpene.

Determination of the terpinolene content. The decrease of the optical rotation of the end fractions of monocyclic terpenes was caused by the presence of terpinolene and small quantities of γ-terpinene in them. The calculation of the terpinolene content in the individual fractions obtained on distillation was made from the $[\alpha]_D$ values of these fractions. All the optically inactive terpenes contained in the fractions after the fraction with a maximum optical rotation were considered to be terpinene. The presence of γ-terpinene was neglected in the calculations. This did not lead to significant errors in the analysis of the monocyclic terpenes isolated from isomerizates containing unreacted pinene, since the γ-terpinene content in them was very small. Since the γ-terpinene content in the monocyclic terpenes increased simultaneously with an increase of the α-terpinene content, a somewhat elevated result of the determination of terpinolene (3-5% according to an approximate calculation) was obtained only for the isomerizate which contained no pinene (see Table, Experiment 5).

The richest terpinolene fraction had the following properties: d_4^{20} 0.8617, n_D^{20} 1.4906, tetrabromide with a m.p. of 117°.

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[*] It was calculated from the proportion $\alpha_D = \frac{29.6 \cdot 126}{53}$, where 126° — $[\alpha]_D$ was optically pure limonene [8, 9], 53° — $[\alpha]_D$ was optically pure pinene [10], 29.6° — $[\alpha]_D$ was the initial pinene.

SUMMARY

1. It was demonstrated that, on heating with titanic acid, a direct conversion of pinene to terpinolene, and also of pinene and limonene to α-terpinene occurred, without the formation of limonene as the intermediate product in the first instance and of terpinolene as the intermediate product in the second.

2. The direct conversion of pinene and limonene to α-terpinene without the formation of terpinolene as the intermediate product became apparent only on consideration of the reaction studied from the ionic point of view, i.e., by assuming the formation from pinene (or limonene) of carbonium ion, which was converted further to limonene, terpinolene and the terpinenes.

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* T. p. = C. B. Translation pagination.

7

POLYMERS OF AMINO ACIDS

(Preliminary Report)

L. N. Akimova and N. I. Gavrilov

In the literature there are repeated indications of an analogy in the properties of polyamino acids and proteins. We tried to observe such an analogy in the behavior of polyamino acids with respect to proteolytic enzymes and in a comparison of their molecular weights with those of the proteins. Moreover, we attempted to find a similarity in the physical properties of the polymers and proteins. Precisely in an attempt to identify the polymers with proteins, we also elucidated the attempt of synthesis of the polymers which was carried out by Woodward and Schramm [1]. In the authors' opinion the polymer which they synthesized was a protein analog. However, in all these investigations and results a simplified and mechanical approach to the most important problem of natural science – the problem of the structure and synthesis of protein – was overlooked.

Studying the action of proteolytic enzymes on polyamino acids of high molecular weight, a number of authors attempted to secure some information of the chemism of the action of these enzymes on proteins [2]. The first enzymatic investigations with polyamino acids were made in 1939 [3]. In these investigations the action of erepsin, papain and tripsin on the water-insoluble polymers of glycine and glycyl-leucine was studied. The enzymes, however, did not act on the polyamino acids. An especially careful fermentation was studied with water-soluble poly-l-lysine. As a result, the extraordinary resistance of such a polymer toward different enzyme systems [4] (carboxypeptidase, pepsin) was recorded. Material on the study of the action of enzymes which cleave proteins, and their capacities to hydrolyze the water-soluble polyamino acids, is exhausted by the foregoing. We assume that even these investigations indicate sufficiently the different structural nature of the polymers, and not only of the proteins, but also of the plasteins obtained synthetically from peptones. In the problem of the similarity and difference of the structure of the proteins and the polymers, the determination of the size of the particles of both is of greatest interest. Moreover, it is necessary to observe that the essential problem of the magnitude of the molecular weight of the polyamino acids has not until now been solved even to a first approximation. Thus, Woodward and Schramm [1] in their first works assumed that the molecular weight of the polymers which they obtained amounted to several millions. Later investigators [3, 5, 6] reduced the assumed size of the polymer molecules considerably, and at present it is necessary to assume it to be close to 6000 (from glycine polymer). Such a striking difference of the sizes of the molecules of polyamino acids from those of proteins and, particularly, the ease of formation of the former, compels us to seek an explanation in the conditions of formation of the molecules. The fundamental difference of a polymerization reaction from that of the synthesis of a protein includes the fact that the synthesis of a protein proceeds in vivo in an aqueous medium, whereas all polymerization reactions take place only in a medium containing traces of water.

Thus, the formation of polyamino acids (organic solvent) is extremely simple compared with that of a protein, the synthesis of which, first, is conditioned by the life process itself; second, requires an unusual medium and, finally, third, the participation of catalysts (enzymes) is required.

Investigations of the physical properties of polyamino acids by means of x-ray structural analysis and spectrophotometry in the infrared region are also of interest. On the basis of the results of these investigations, a large number of authors reached a conclusion concerning the protein nature of the polymers. Thus, by an x-ray investigation of the polyglycine obtained by the polymerization of N-carboxyglycine anhydride, Meyer and Go [5] observed that the fundamental ranges of this polymer lie in areas separated by a distance of 4.15 A. A similar investigation of β-keratin enabled the authors to identify polyglycine with β-keratin. From a comparison of the absorption spectra in the infrared region for the polyamino acids and for the proteins, it was concluded [7] that the definite frequencies characteristic of each amino acid in the polymer are retained also in the proteins which contain these amino acids.

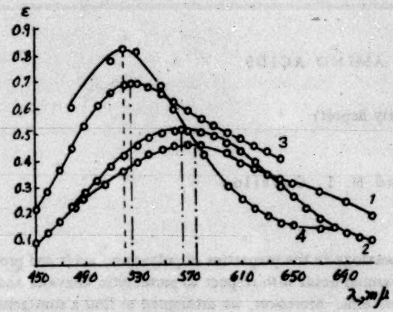

Fig. 1. Spectrophotometric curves of biuret cupric complexes.
1) Tripeptide (1/150 M solution); 2) gelatin (0.25% solution); 3) polyglycine (0.14% solution); 4) tetrapeptide (1/150 M solution).

A series of authors [8] used polyglycine as a model for the determination of the quantity of water absorbed by protein for one peptide bond at different relative humidities. The absorption of water by the polyglycine polymer obtained by two different methods was the same in spite of their different average molecular weights; but this absorption of water by both glycine polymers [6, 9] considerably exceeded the absorption by tetra-, penta- and hexa- glycine, which should be expected from the point of view of a change of the quantity to a new character. Moreover, the quantity of absorbed water calculated for 1 mole of the polymer on the basis of the number of free amine and ester groups, was considerably less than the observed value. Owing to the fact that silk absorbs the same quantity of water as polyglycine, the authors concluded that there is a different number of polar groups in the structure of the silk and in that of polyglycine.

Proceeding from the above-cited observations, it seemed to us also that the forces which control the synthesis of the polyamino acids, are probably similar to those which lead to the organization of a large protein molecule. However, from the very beginning, our investigations of the polymers showed that we were incorrect in our assumption that, not only the molecular weight and a number of physical properties (solubility, etc.) distinguished the proteins from the polyamino acids, but that also the structure of these molecules themselves differed basically from each other.

The biuret reaction, so characteristic of proteins, showed the definite presence of peptide structures both in proteins and in the polyamino acids. Visually, the cupric complexes of polyamino acids hardly differ in color from those of the proteins, particularly the protamines. However, a spectrophotometric investigation of the cupric complexes of the peptides of proteins and polyamino acids (Fig. 1) indicated their essential difference which, obviously, also depended on the internal structure of the molecule.

As is known, the spectrophotometric curves of solutions of the biuret cupric complexes of proteins have an absorption maximum in the wavelength range of 540-565 mμ. The determination of copper in the cupric complexes of proteins [10],and the total course of the curve of these complexes with a characteristic maximum, forces us to assume as correct the hypothesis which we put forth earlier concerning the tripeptide nature of the structure of the linear portion of the protein structure. The spectrophotometric curves of glycine polymers obtained by different methods, unlike those of the proteins, have an absorption maximum at 525 mμ. This fact relates the cupric complexes of the polymers to those of the octa- and tetra- peptide (maximum 520-525 mμ) [11]. Like the proteins, the copper number of which indicated their tripeptide character, the determination of copper in the cupric complexes of the polymers corresponded to their tetrapeptide content (accordingly, octapeptide; Table 2).

In spite of such a completely expected similarity, the absorption spectrum of polyglycine also has an essential difference from that of the octapeptide (or tetrapeptide) (Fig. 2). This difference includes the fact that in the long-wave part of the spectrum of about 610-620 mμ we have considerable light absorption which, being superimposed on the fundamental red color, gave a visual violet color.

What are the considerations which condition the increase of light absorption in this region? We offer the following tentative hypotheses:

1) water of hydration, undoubtedly present in the polyamino acid molecule, and possibly bound with definite, regularly recurring structures, gives a condition for the formation of the additional absorption of such an intricate complex. It is necessary to observe that not only the absorption maximum at 525 mμ indicates the characteristic octa-tetrapeptide structure of such a complex, but also the copper number determined by the whole structure of the complex indicates the presence of octapeptide fragments in the polymers;

2) the increase of the intensity of light absorption in the long-wave region, i.e., in the 610-620 mμ region, indicates the presence of some additional groups, close in their character to dipeptide, which affect this increase (the absorption maximum of the dipeptides is at 610 mμ). Such an intensity increase was explained by one of us

(N. I. Gavrilov) by the possible existence in the polyamino acid structures of dipeptide fragments, which are not fragments of the main polymer chain. By analogy with starch, they may represent side chains to the basic valence chain of the polymer. The empirical formula of any polymer is packed into a tetrapeptide fragment of anhydride arrangement. According to analytical data, and to the absorption maximum of its copper complex, the glycine polymer which we obtained corresponded to the octapeptide. We can represent the structure of such a polymer as an octapeptide with a molecular weight of 474, combined n times $(C_{16}H_{26}O_9N_8)_n$.

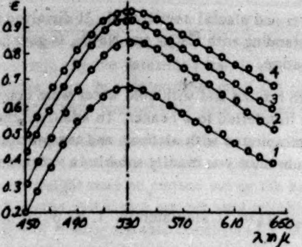

Fig. 2. Spectrophotometric curves of biuret cupric complexes of 0.14% solutions of glycine polymers obtained under different conditions.
1) In water; 2) in organic solvent; 3) in presence of enzyme; 4) in production of diketopiperazine.

The presence of the piperazine ring in the structure of a protein seems to be most important in conditioning its physiological functionality. All proteins contain approximatedly from 25-40% of the cyclic forms of bonds (from α-amino nitrogen) between the amino acids. And it is natural that, in the first place, we attempted to find these forms of bonds also in the polyamino acids. The picric reaction, observed by a whole series of investigators for polyamino acids, did not appear to be their structural reaction, because the anhydride reaction was absent after treatment of a majority of the polyamino acids with hot water (with the exception of the polymer obtained in an organic solvent). It is necessary to note again that the washing filtrates, from the treatment of the polyamino acids with water, developed a red biuret reaction, which indicated the presence in them of tetrapeptides or peptides of multiple length.

Experiments with the electroreduction of the polyamino acids showed a complete absence in their structure of the cyclic form of bonds of the amino acids. The polyamino acids were not fermented by pepsin. Thus, it was now possible to state definitely that the structure of the polyamino acids differed essentially from the protein structure. This difference was so great that it was impossible even to consider the polyamino acids as protein-like compounds. Nevertheless, clarification of their structure, and especially establishment of the order and character of the reactions leading to their formation, may also shed light on the structure of protein.

EXPERIMENTAL

N-carboglycine anhydride (Leuchs' anhydride) [12] was used for the production of the glycine polymers.

1. Synthesis of N-Carboglycine Anhydride *

6.3 g of carbobenzoxyglycine with 35 ml of anhydrous ether, and 6.7 g of powdered PCl_5 was shaken, with cooling, until all had dissolved (approximately 20 minutes). The liquid, filtered at reduced pressure and 10°, was evaporated until the formation of a viscous oil as the residue, which was treated twice with dry petroleum ether. On the addition of a third portion of petroleum ether, and on cooling to −10°, the oil crystallized. The substance which formed was filtered off and washed with ether and with alcohol. According to the analysis it was the inner anhydride of N-carboglycine. Its yield was 2.7 g.

2. Production of the Glycine Polymers

a) In water at room temperature. A twofold quantity of water (2 ml) was added to 1.0 g of carboglycine anhydride, obtained by the above-described method; moreover, strong frothing and evolution of CO_2 resulted. After 10 minutes the precipitate was filtered off and washed on the filter, first with cold water (in the aqueous filtrate there was a red biuret reaction and a negative anhydride reaction), and then with hot water (in the filtrate there was a violet biuret reaction and a negative anhydride reaction). We continued the treatment of the precipitate with boiling water until there was a negative biuret reaction in the filtrate, after which the precipitate was washed with alcohol,

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* It is best to obtain Leuchs' anhydride by a method described for the acid chloride of carbobenzoxyglycine. As shown experimentally, an increase of the quantities of the starting materials by a factor of 2 reduced the yield by a factor of 2.

Found %: C 40.20, 39.92; H 5.66, 5.83; N 22.24, 22.19 $(C_{16}H_{26}O_9N_8)_n$. Calculated %: C 40.51; H 5.49; N 23.62.

Properties. It was insoluble in boiling water, organic solvents and glacial acetic acid. It dissolved in concentrated hydrochloric and in 100% formic acids. On 30-minute standing with $CuCl_2$ and NaOH, it gave a positive biuret reaction of a violet color. The anhydride reaction was negative.

The aqueous filtrates from the treatment of the polymer with boiling and with cold water were concentrated to dryness in vacuo. With a stream of cold water, the residue was transferred to a beaker. In addition, the polymer precipitate which came down was filtered off. The filtrate was precipitated with alcohol; and the precipitate was filtered off and washed on the filter with alcohol. The resulting substance was readily soluble in water, and insoluble in alcohol. It gave a biuret reaction with a red hue.

Found %: C 37.29, 37.37; H 6.30, 6.06; N 21.72, 21.68. $C_6H_{11}O_4N_3$. Calculated %: C 38.00; H 5.9; N 22.2. $C_8H_{14}O_5N_4$. Calculated %: C 39.97; H 5.69; N 22.6.

On comparison of the properties and analytical data of this substance with those of the tri- and tetrapeptides, it followed that the substance which we isolated was a mixture of the tri- and tetrapeptides of glycine (an admixture of peptides of greater length was also possible).

b) In an organic solvent with heating. 20 ml of xylol was added to 1.7 g of N-carboglycine anhydride, and it was heated with Wood's alloy for 45 minutes. The decomposition of the anhydride and, as a result of this decomposition the formation of the polymer, took place only at 100°, and therefore only a solvent with a b.p. of 100° or more could be used for this purpose. On completion of the reaction (after 45 minutes), the precipitate was filtered off and washed with xylol. Completion of the reaction was judged by the cessation of the evolution of CO_2 (by reaction with baryta water). The polymer yield was 0.9 g, i.e., it was quantitative. The substance was treated with boiling water for analysis.

Found %: C 40.41, 40.50; H 5.70, 5.74; N 23.16, 23.19. $(C_{16}H_{26}O_9N_8)_n$. Calculated %: C 40.51; H 5.49; N 23.62.

Properties. It was insoluble in boiling water, organic solvents and glacial acetic acid; it was poorly soluble in concentrated hydrochloric acid; it was soluble in 100% formic acid on heating; it dissolved in alkali only on standing for several hours in the presence of copper. The biuret reaction was of a violet color. The anhydride reaction was positive.

c) Investigation of the polymer isolated in the synthesis of diketopiperazine. In the synthesis of diketopiperazine from the hydrochloride of the methyl ester of glycine and NaOH, according to Fischer a glycine polymer was isolated as a by-product. The treatment of this polymer was similar to that described in Experiments "a" and "b".

Properties. It was insoluble in boiling water, organic solvents and glacial acetic acid; it was insoluble in alkali and dissolved in it only on addition of a copper solution, upon which a red biuret reaction appeared instantly; it was soluble in concentrated hydrochloric and in 100% formic acids in the cold. The biuret reaction was positive; the anhydride reaction, with long heating, was negative. The analytical data of such a polymer yielded uncertain results. *

3. Investigation of the Structure of the Glycine Polymers

a) Electroreduction of the polymer obtained in an aqueous medium (carried out by P. G. Ioanisian). 0.1038 g of polyglycine was dissolved in 100 ml of concentrated hydrochloric acid, and 60 ml of distilled water and approximately 30 ml of concentrated hydrochloric acid (washing) were added. The temperature of the solution did not rise above 25°, and after external cooling it fell to 11-12°, and then during the electroreduction rose to 25°. The electroreduction was continued for 7 hours. The reduced polymer, together with the washing waters, was concentrated in vacuo to a small volume. The residue was boiled under reflux with 40 ml of concentrated hydrochloric acid for 20 hours. After the acid hydrolysis the solution was concentrated to dryness in vacuo. Several drops of 20% alkali, and then 0.2 N NaOH, was added to the residue in the flask until there was a neutral reaction to neutral red. Then, adding 10 ml of a formol mixture, it was back-titrated according to Sörensen-Gavrilov.

0.1038 g sub.: 14.32 ml 0.1 N H_2SO. Found %: NH_2-group 19.31. 0.1038 g sub.: 14.54 ml 0.1 N H_2SO_4. Found %: N 19.61.

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* It is probably a mixture of polymers of different length.

The equality of the quantity of amine nitrogen after reduction (19.31%) and the total nitrogen (19.61%) indicated the absence of piperazine in the reduction products.

b) Determination of the amine nitrogen in the polymer obtained in water. Because the polymer was soluble in 100% formic acid in the cold, it was of interest to carry out a determination according to Slyaik with this acid as the solvent. By the determination, it was found that formic acid decomposed the nitrous acid and, therefore, we were unable to make a determination of the amine groups of the polyglycine. A determination of the amine nitrogen in dilute (15%) hydrochloric acid also led to no satisfactory results.

As has already been mentioned, one of the most interesting characteristics of the polymers was their molecular weight. In such compounds as polyamino acids, particularly the glycine polymer, a determination of the molecular weight may be carried out on the basis of a quantitative calculation of the end amine groups. The methods of Sörensen and Slyaik are not very reliable, as a result of the difficult solubility of the polymer, and the impossibility of finding suitable conditions for determination of the amine groups. Following Experiment "3b", we decided to carry out an amine nitrogen determination in the polymer with hydrochloric acid, by the equivalent free amine groups after esterification of the polymer with ethyl alcohol.

c) Esterification of the polymer (obtained in water). 25 ml of anhydrous ethyl alcohol was added to 0.75 g of the polymer, and saturated with dry hydrogen chloride for 2.5 hours in the cold, and then for 3 hours with heating. The precipitate did not dissolve. After cooling, the precipitate was filtered off, washed with alcohol and dried over alkali and calcium chloride in a vacuum-desiccator. The substance, containing halide, was analyzed for its amine nitrogen content according to Sörensen-Gavrilov.

0.3660 g sub.: 5.08 ml 0.1 N NaOH. 0.3660 g sub.: 5.35 ml 0.1 N H_2SO_4. Found %: C 40.17, 40.26; H 5.80, 5.90; N 20.93. $C_{18}H_{30}O_9N_8 \cdot HCl$. Calculated %: C 40.12; H 5.75; N 20.80.

The quantity of hydrochloric acid found was equal to 5.3%, which corresponded to 2.1% amine nitrogen in the polymer. The amine nitrogen, calculated for the hydrochloride ester of the octapeptide, amounted to 2.6%.

d) Preparation of cupric biuret solutions of the polymers. 15 ml of a 2% solution of $CuCl_2$ and 15 ml of a 2% solution of NaOH were added to a weighed portion of 100-150 mg of the polymer. The solution was mixed by shaking for from 1 hour to several hours (in the case of the polymer obtained in the organic solvent), and was centrifuged after a definite time. The clear solution of the copper complex of the polymer was used for spectrophotometry. 0.14% solutions (according to the polymer) of the cupric complexes were usually prepared. We used an SF-4 spectrophotometer for taking the spectrophotometric curves. The results of the spectrophotometry of the polymer complexes obtained under different conditions are presented in Table 1 and Fig. 2.

e) Determination of copper in biuret cupric solutions of polymers. The biuret cupric solution of the polymer was centrifuged and from 10 to 30 ml of the clear solution of the copper complex, containing from 50 to 150 mg of the original polymer, was used. After decomposition of the copper complex with 2N sulfuric acid* the copper in the solution was determined iodometrically (Table 2).

The theoretical copper number for the octapeptide (tetrapeptide) was equal to 246. The experimental values of the copper number of the polymers were equal to 236 on the average.

4. Production of Polymers in the Presence of Gastric Juice

The activity of gastric juice on plastein formation was verified on Witte peptone. For this, 3 g of the peptone was dissolved in 9 ml of water. A pH of 4.5 was assumed to be the optimum condition of the medium for plastein formation. 20 ml of gastric juice was added for reduction of the pH of the peptone solution from 7.5 to 4.5. After 1 hour of standing in a thermostat ** a precipitate came down, which was centrifuged; the solution was decanted, and it was washed 2 times with water. The precipitate gave a biuret reaction of a protein nature (without traces of red), whereas the solution which was poured off from the precipitate gave only a red biuret reaction. Plastein formation proceeded much faster with the action of gastric juice on an aqueous solution of the peptone than with the action of pepsin on the peptone solution.

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* Determination of the copper in solution was made both before and after combustion with H_2SO_4. The results of the determinations agreed. Regeneration of the polymer took place on decomposition of the copper complex with sulfuric acid.

** An appreciable turbidity was observed on addition of a completely clear gastric juice to a well-centrifuged aqueous solution of the peptone.

TABLE 1

Spectrophotometric Curves of 0.14% Solutions of Biuret Cupric Complexes of Different Polymers

λ (in mμ)	Values of the optical densities					
	aqueous polymer	polymerization in the presence of			polymer obtained in organic solvent	polymer of diketopiperazine
		gastric juice, unneutralized	gastric juice + CH_3COONa	gastric juice + glycine		
450	0.213	0.210	0.179	0.202	0.185	0.209
460	0.284	0.281	0.254	0.286	0.258	0.278
470	0.371	0.374	0.340	0.381	0.343	0.360
480	0.461	0.473	0.430	0.478	0.439	0.447
490	0.544	0.561	0.505	0.561	0.534	0.524
500	0.611	0.633	0.572	0.636	0.607	0.591
510	0.661	0.689	0.620	0.690	0.654	0.647
520	0.681	0.713	0.642	0.719	0.695	0.677
525	0.693	0.727	0.658	0.736	0.695	0.690
530	0.683	0.722	0.655	0.733	0.683	0.686
540	0.677	0.707	0.651	0.731	0.666	0.679
550	0.634	0.676	0.636	0.722	0.643	0.663
560	0.617	0.656	0.597	0.672	0.610	0.630
570	0.586	0.624	0.569	0.640	0.583	0.591
580	0.553	0.589	0.540	0.608	0.554	0.556
590	0.525	0.557	0.517	0.579	0.537	0.516
600	0.501	0.523	0.492	0.549	0.515	0.474
610	0.481	0.496	0.466	0.516	0.505	0.430
620	0.447	0.458	0.440	0.481	0.488	0.391
630	0.431	0.427	0.412	0.447	0.469	0.360
640	0.399	0.392	0.384	0.411	0.433	0.315

TABLE 2

Copper Numbers of the Polymers

Origin of polymer	Conditions of formation of copper complexes	Quantity of polymer (in g)	ml 0.05 N solution of $Na_2S_2O_3$ consumed	Copper number
obtained in water	deficiency of copper	0.0573 in 22 ml	4.7	249.7
obtained in water	ordinary conditions	0.0294 in 15 ml	2.65	221.7
obtained in water	ordinary conditions	0.0261 in 10 ml	2.35	222.1
obtained in water	ordinary conditions	0.0507 in 25 ml	4.61	220.3
obtained in water	after 1 day of standing with 10% solution of NaOH	0.0718 in 20 ml	4.80	299.3
polymer hydrochloride from Experiment "c"	ordinary conditions	0.0784 in 25 ml	6.76	233.3
from Leuchs' anhydride in an organic solvent	weighed portion dissolved in conc. HCl. Added: 2% $CuCl_2$ and 20% NaOH, with cooling	0.0445 in 15 ml	3.8	234
from Leuchs' anhydride in an organic solvent	cupric complex prepared by usual method and left overnight with $Cu(OH)_2$	0.0949 in 30 ml	7.6	262.8
polymer of diketopiperazine	ordinary conditions	0.0651 in 15 ml	5.22	249.3
polymer obtained from Leuchs' anhydride in a gastric juice medium	ordinary conditions	0.1464 in 15 ml	11.97	244.0
polymer obtained from Leuchs' anhydride in a gastric juice medium	ordinary conditions	0.0976 in 10 ml	8.12	240.4

Production of the polymers. Similar polymer precipitates were obtained by the action of gastric juice on Leuchs' anhydride without the introduction of buffer, and also with the establishment of a pH of 4.5 by means of sodium nitrate and glycine.

We conducted the following experiment in order to elucidate the mechanism of formation of the polymers (whether it proceeds via the stage of cyclization of the tripeptide to N-glycine diketopiperazine, or whether it is connected with a linear polymerization of a chain character). Assuming that one of the intermediate stages in the synthesis of the polymers was the formation of diketopiperazine or its derivative, we decided to accelerate the polymerization process. For this we added diketopiperazine at the moment of formation of the polymer from Leuchs' anhydride. 2 g of Leuchs' anhydride was added to the solution containing 0.15 g of diketopiperazine in 4 ml of water. 5 minutes after addition of the anhydride strong frothing and evolution of CO_2 began, which was stopped after 15 minutes. The precipitate was filtered off and treated, first with cold, and then with hot, water. Moreover, the yield of the polymer was 1.1 g, i.e., it was quantitative. 0.12 g of diketopiperazine was separated from the filtrate by concentration. The diketopiperazine which obviously did not take part in this reaction, was recovered as a result of the reaction carried out.

Discussion of Results

The principal difference in the behavior and properties of proteins and the polymers can be observed on the basis of the investigation made. This difference includes the facts that:

1) in all proteins studied thus far; from 25 to 40% of the amino acids are cyclized to piperazines;

2) the investigation of the absorption spectra of the cupric biuret complexes of the proteins indicated the predominance of "violet" complexes (46-85%) in their structure [10]; "red" copper complexes comprised only a small per cent in protein (15-54%);

3) in the vast majority of cases the proteins have the capacity to dissolve in water (albumins), in alcohol (glutelins), and in concentrated salt solutions (globulins), whereas the polymers are insoluble in these solvents, and dissolve with difficulty in concentrated acids and alkalis.

The polymers differ sharply from the proteins by the following:

1) the complete absence of cyclic forms of bonds between the amino acids; only in the polymer formed in an organic solvent (xylol) did we observe a negligible presence of cyclic forms of bonds, not exceeding 8%;

2) the polymers contained, depending on the length of the peptide, up to 2% of amino nitrogen, whereas the proteins did not have end α-amino acid groups.

The cupric biuret complexes were the most interesting of all the properties of the polymers. An analysis of the absorption spectra of the cupric biuret complexes of the polymers indicated their great difference from the proteins. The absorption spectra of the cupric complexes of the proteins were characterized by the presence of those structures which give complexes with copper, formed by four nitrogen atoms (on the average 30%), and are characterized by a quite definite absorption maximum (540-565 mμ), with a very sharp reduction of the intensity of absorption in the long-wave region.

An analysis of the absorption spectra by the cupric complexes of the polymers quite definitely indicated the existence of a fundamental maximum at 525 mμ, with considerable absorption in the long-wave region, which also affected the visual color of these solutions (violet).

Whereas the copper number of the proteins quite clearly showed the tripeptide character of the individual fragments, the cupric complexes of the polymers differed exactly by tetrapeptides and peptides, by a multiple of 4 (8-, 12-, 16-, etc.). The polyglycine from Leuchs' anhydride which we studied was an octapeptide. Since it differed from the synthetic octapeptide in solubility and in the absorption spectra of the cupric complexes, it is necessary to assume that it underwent further association to a molecule of considerable size.

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* T. p. = C. B. Translation pagination.

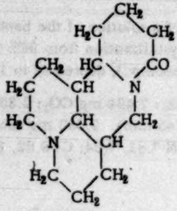
THE ALKALOIDS FROM *SOPHORA PACHYCARPA*

A NEW ALKALOID – PACHYCARPIDINE

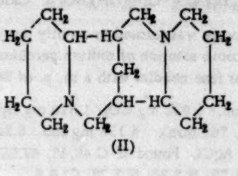
M. S. Rabinovich

Sophora pachycarpa, thick-pistilled *Sophora* (bean family), is an alkaloidal plant which is widely distributed in Central Asia, the study of which was begun in 1933 by A. P. Orekhov and his coworkers. The new alkaloid, sophocarpine, and the earlier-described matrine (I) were isolated from the seed of this plant by Orekhov and Proskurnina [1]. Together with sophocarpine and matrine, a new alkaloid, pachycarpine (II), which is apparently the dextrorotatory form of lupinidine, was isolated from the stems and leaves of *Sophora pachycarpa* by Orekhov, Rabinovich and Konovalova [2].

In connection with the introduction of pachycarpine to medical practice, the attention of investigators has again been focused on the chemical study of this widely available plant, the total alkaloid content of which amounts to 2-2.5% of its dry weight. In 1953 Proskurnina and Kuzovkov [3] isolated still another crystalline alkaloid – sophoramine, described earlier as a base from *Sophora alopeeuroides* – from the above-ground parts of thick-pistilled *Sophora*. They established that sophocarpine and sophoramine form matrine on catalytic reduction. Thus, the alkaloids of *Sophora pachycarpa* isolated until now belong to two different heterocyclic systems.



(I)



(II)

By further study of the alkaloids of thick-pistilled *Sophora* by using the ion-exchange adsorption method, we were able to separate from an aqueous extract of the plant one more crystalline base with a m. p. of 177-179°, $[\alpha]_D + 26.6°$, which forms a crystalline picrate with a m. p. of 210-211° and a crystalline pechlorate with a m. p. of 204-205°. According to an elementary analysis of both the base and its salts, the composition of the base $C_{15}H_{22}N_2O_2 \cdot H_2O$ was established. Since the newly isolated alkaloid differed in its properties from the bases described in the literature, we named it pachycarpidine.

Pachycarpidine was readily reduced by zinc dust in sulfuric acid solution, forming an oxygen-free liquid base, desoxypachycarpidine, from which the following were obtained: a crystalline picrate of composition $C_{15}H_{22}N_2 \cdot (C_6H_3O_7N_3)_2$ with a m. p. of 128-130°, and a hydriodide of composition $C_{15}H_{22}N_2 \cdot HI \cdot H_2O$ with a m. p. of about 280°.

Such a simple formation of an oxygen-free substance, together with the absence in pachycarpidine of hydroxyl, methoxyl and N-methyl groups, enabled us to assume that both nitrogen atoms of this alkaloid occur in the form of oxide groupings similar to those which occur in trilupine [4]. This assumption was confirmed by the production of the original pachycarpidine from desoxypachycarpidine by oxidation with hydrogen peroxide.

EXPERIMENTAL

Isolation of Pachycarpidine

2 kg of the above-ground parts of the plant was drenched with a 2% solution of sulfuric acid. After 18-20 hours the extract (as a viscous syrup) was diluted with an equal volume of water, after which it was filtered through a

column filled with Espatite-I, first converted to the H⁺-form. Moreover, the alkaloids were completely absorbed by the H⁺-cationite. The desorption of the alkaloids was carried out with a 20% solution of ammonia in methyl alcohol. After vacuum evaporation of the resulting filtrate the residue was dissolved in 10% sulfuric acid. The acid solution was washed repeatedly with benzene in order to remove the resinous, weakly-basic impurities, then it was saturated with a 40% solution of sodium hydroxide, and extracted with chloroform. After evaporation of the solvent the residue crystallized; 16 g of a crystalline, slightly oily base was obtained, which was readily soluble in water, insoluble in ether, and difficultly soluble in acetone. After dissolving it in hot acetone (1:20), and after evaporation of the latter to 1/3 of its original volume, the pachycarpidine crystallized. During the determination of the melting point the base melted at 140-150°, then solidified again and melted at 177-179°.

Pachycarpidine was also isolated by extraction of the above-ground parts of Sophora pachycarpa with isopropyl alcohol. The alkaloids obtained from 1 kg of the plant were dissolved in dilute sulfuric acid, and after treatment with benzene the acid solution was saturated with a 40% solution of sodium hydroxide, extracted with ether, and then extracted with chloroform. 12 g of pachycarpidine was isolated from the ether fraction and 7 g of pachycarpidine was obtained from the chloroform fraction; $[\alpha]_D + 26.6°$.

3.057 mg sub.: 7.128 mg CO_2; 2.350 mg H_2O. 4.568 mg sub.: 10.711 mg CO_2; 3.581 mg H_2O. 6.965 mg sub.: 0.637 ml N_2 (23.0°, 739 mm). 8.150 mg sub.: 0.733 ml N_2 (24.0°, 738 mm). Found %: C 63.59, 63.94; H 8.60, 8.77; N 10.25, 10.05. $C_{15}H_{22}N_2O_2 \cdot H_2O$. Calculated %: C 64.2; H 8.57; N 10.0.

Salts of Pachycarpidine

The picrate was formed as an oily residue by mixture of alcoholic solutions of the base and picric acid. After recrystallization from ethyl acetate its m. p. was 210-211° (with decomp.).

4.650 mg sub.: 8.740 ml CO_2; 2.219 mg H_2O. 3.411 mg sub.: 6.444 mg CO_2; 1.551 mg H_2O. 3.950 mg sub.: 0.520 ml N_2 (23°, 735 mm). 5.590 mg sub.: 0.718 ml N_2 (24.5°, 738 mm). Found %: C 51.26, 51.52; H 5.33, 5.09; N 14.65, 14.30. $C_{15}H_{22}N_2O_2 \cdot C_6H_2(OH)(NO_2)_3$. Calculated %: C 51.32; H 5.09; N 14.2.

The perchlorate was formed as an oily powder by mixture of a solution of the base in 10% hydrochloric acid and a saturated aqueous solution of sodium perchlorate. After recrystallization from 96% alcohol (1:10) the perchlorate was obtained as fine needles with a m. p. of 204-205° (with decomp.), depressed to 180°).

3.320 mg sub.: 6.022 mg CO_2; 1.810 mg H_2O. 4.061 mg sub.: 7.424 mg CO_2; 2.339 mg H_2O. 7.120 mg sub.: 0.493 ml N_2 (24.5°, 744 mm). 4.115 mg sub.: 0.249 ml N_2 (23°, 745 mm). 7.633 mg sub.: 3.031 mg AgCl. 5.673 mg sub.: 2.352 mg AgCl. Found %: C 49.47, 49.85; H 6.10, 6.44; N 7.81, 7.94; Cl 9.82, 9.74. $C_{15}H_{22}N_2O_2 \cdot HClO_4$. Calculated %: C 49.72; H 6.35; N 7.73; Cl 9.8.

Reduction of Pachycarpidine

3 g of zinc dust was added gradually (during 1 hour) to a solution of 3.3 g of pachycarpidine in 20 ml of 10% sulfuric acid, with mechanical stirring. After 1.5-2 hours the excess of zinc dust was filtered off, and the filtrate was saturated with a 40% solution of sodium hydroxide and extracted with ether. 2.6 g of desoxypachycarpidine, as a light, mobile oil, remained after evaporation of the ether.

Salts of Desoxypachycarpidine

The picrate was formed as an oil by mixture of alcoholic solutions of the base and picric acid. On addition of acetone the picrate was converted to a solution from which, on standing, it crystallized; its m. p. was 128-130°.

4.160 mg sub.: 7.090 mg CO_2; 1.468 mg H_2O. 3.609 mg sub.: 6.172 mg CO_2; 1.323 mg H_2O. 4.245 mg sub.: 0.622 ml N_2 (23°, 745 mm). 4.030 mg sub.: 0.586 ml N_2 (23.0°, 745 mm). Found %: C 46.48, 46.64; H 3.95, 4.13; N 16.56, 16.43. $C_{15}H_{22}N_2 \cdot [C_6H_2(OH)(NO_2)_3]_2$. Calculated %: C 47.09; H 4.06; N 16.27.

The hydriodide was obtained as a yellowish powder by the addition of hydriodic acid to a solution of the base in acetone.

Its m. p. was ~280° after recrystallization from 96% alcohol.

8.256 mg sub.: 13.26 ml 0.01 N $Na_2S_2O_3$. 6.745 mg sub.: 10.73 ml 0.01 N $Na_2S_2O_3$. Found %: I 33.98, 33.66. $C_{15}H_{22}N_2 \cdot HI \cdot H_2O$. Calculated %: I 33.77.

Oxidation of Desoxypachycarpidine

0.35 g of the base was mixed with 2 ml of a 27% solution of H_2O_2 and 2 ml of water. The base dissolved after standing for 3 days, and the excess H_2O_2 was removed in vacuo. The residue was dissolved in chloroform, the extract was dried, and the solvent was removed. The resulting base crystallized on treatment with acetone. A sample of a mixture of the resulting base with pachycarpidine showed no melting point depression.

SUMMARY

1. A new crystalline alkaloid, named pachycarpidine, of composition $C_{15}H_{22}N_2O_2 \cdot H_2O$, was isolated from the above-ground part of Sophora pachycarpa (thick-pistilled Sophora).

2. By reduction of pachycarpidine with zinc dust in sulfuric acid solution, an oxygen-free base $C_{15}H_{22}N_2$ was obtained, which on oxidation with hydrogen peroxide yielded the original pachycarpidine.

3. Both of the oxygen atoms of pachycarpidine occurred as N-oxide groupings.

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reaction for 8 days, and the excess H_2O_2 was removed in vacuo. The residue was dissolved in chloroform, the extract was dried, and the solvent was evaporated [illegible] crystallized on standing. [illegible] mixture of the resulting base with pachycarpine [illegible] no depression of melting point.

SUMMARY

1. A new alkaloid [illegible] compound C [illegible] isolated from the above-ground part of Sophora pachycarpa. [illegible]

2. By reduction of pachycarpine [illegible] with zinc dust in [illegible] an oxygen-free base [illegible] obtained, which on oxidation with hydrogen peroxide yields the original [illegible]

3. Both of the [illegible] of pachycarpine [illegible]

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SYNTHESIS OF ORGANO-ELEMENTARY COMPOUNDS OF THE ALIPHATIC SERIES BY THE DIAZO METHOD

VI. SYNTHESIS OF COMPOUNDS OF THE ELEMENTS OF GROUP V – ORGANOPHOSPHORUS COMPOUNDS. TRICHLOROMETHYLPHOSPHINIC ACID AND ITS DERIVATIVES

A. Ya. Yakubovich and V. A. Ginsburg

In a previous report [1] it was shown that the reaction of aliphatic diazo compounds with the phosphorus halides can serve as a convenient method of synthesis of the α-alkyl halide derivatives of phosphorus. For example, chloromethyldichlorophosphine was obtained in this way.

On attempt to obtain phosphorus chloromethyltetrachloride from it by chlorination in CCl_4 in the cold with an excess of chlorine, it was found that the resulting product was not the substance expected, but was a compound of a composition corresponding to the formula CCl_3PCl_4.

Thus, the reaction of chloromethyldichlorophosphine with an excess of chlorine proceeded according to the scheme:

$$ClCH_2PCl_2 \xrightarrow{Cl_2} ClCH_2PCl_4 \xrightarrow{Cl_2} Cl_2CHPCl_4 \xrightarrow{Cl_2} Cl_3CPCl_4.$$

The bromination reaction of $ClCH_2PCl_2$, which can be stopped easily at the chlorobromomethyldichlorodibromophosphoric derivative $ClBrCHPCl_2Br_2$ stage, proceeds exactly the same, but more slowly.

Such ease of chlorination of the chloromethyldichlorophosphine organic radical is explained, on the one hand, by the presence of a chlorine atom in the methyl group which, apparently, is chlorinated more readily than the unsubstituted group, as was also observed, for example, for the methylsilanes [2]; on the other hand, apparently, it is essential that the chlorination of the organic radical in this case proceed in the presence of the $RPCl_4$ compound which, like PCl_5, can catalyze the chlorination process.

The more readily proceeding halogenation of the alkyl radical of the chloromethyldichlorophosphine enabled us also to obtain and to investigate a series of perchloromethyl organophosphorus compounds which were unknown before the beginning of our investigation. Since an acquaintance with the properties of the series of compounds indicated revealed interesting peculiarities in their chemical behavior, a more detailed investigation of these substances was undertaken.

Phosphorus dichloromethyltetrachloride was obtained by the chlorination of chloromethyldichlorophosphine with the calculated quantity of chlorine. This substance was a crystalline compound which was difficultly soluble in CCl_4, and which decomposed on heating. On hydrolysis, hygroscopic dichloromethylphosphinic acid was formed, which was isolated as the monohydrate with a m. p. of 53° (after careful drying – m. p. 115°).

Phosphorus trichloromethyltetrachloride was obtained by chlorination of $ClCH_2PCl_2$ with an excess of chlorine. This consisted of colorless crystals, which dissolved poorly in organic solvents. The substance dissolved slowly in cold water or in a 0.5 N aqueous solution of potassium hydroxide, during which its hydrolysis did not proceed completely; a 1-2 hour boiling of a weighed portion of the substance in an excess of 0.5 N potassium hydroxide led to the splitting off of all seven chlorine atoms of the molecule. By treatment of the tetrachloride with sulfurous anhydride, it was converted to the acid dichloride of trichloromethylphosphinic acid, which was a hygroscopic solid substance, characterized by still greater stability toward hydrolysis.

This acid chloride hydrolyzed very slowly in cold water, and in aqueous 0.5 N caustic potash, for which titration of the hydrolyzate indicated the splitting off of only one halide atom.

Boiling of the substance with alkali for 1-2 hours led to the complete decomposition of the molecule and to the splitting off of all five chlorine atoms.

The low mobility of the second chlorine atom of the acid chloride in this compound appeared also in the production of the anilides. In benzene solution the acid dichloride and aniline readily yielded the monoanilide $CCl_3PO(Cl)NHC_6H_5$. Long (3-5 days) standing of a mixture of CCl_3POCl_2 with an excess of aniline in benzene was necessary for production of the dianilide.

On production of the esters of trichloromethylphosphinic acid by the usual methods, there can be a risk of cleavage of the C–P bond, which may proceed by the action of sodium alcoholate, similar to that which occurred in the series of organosilicon compounds, which readily split off the trichloromethyl group by the action of aqueous alkalies and even water [2]; therefore, the reaction of its acid chlorides with ethyl nitrite was used for production of the ethyl ester of trichloromethylphosphinic acid, for which it was assumed that reaction proceeded according to the scheme:

$$CCl_3POCl_2 + 2C_2H_5ONO \rightarrow CCl_3PO(OC_2H_5)_2 + 2ClNO.$$

However, even under the conditions of a large excess of ethyl nitrite the replacement of halides by the ethoxyl group did not take place completely; therefore, for the purpose indicated above the reaction of ethyl nitrite with CCl_3PCl_4, was studied, as a result of which the diethyl ester of trichloromethylphosphinic acid was obtained according to the reaction:

$$CCl_3PCl_4 + 3C_2H_5ONO \rightarrow CCl_3PO(OC_2H_5)_2 + 3ClNO + C_2H_5Cl.$$

The diethyl ester of trichloromethylphosphinic acid was a colorless liquid with a fruity odor, was readily soluble in organic solvents and was poorly soluble in water. By saponification of the indicated ester by heating at about 150° in a sealed tube with 15% hydrochloric acid and by evaporation of the aqueous solution in vacuo, trichloromethylphosphinic acid was obtained, which after careful drying over P_2O_5 in vacuo, crystallized as needles with a m. p. of 87°. Analyses showed that the acid contained a molecule of combined water, which could be removed neither by careful drying of the substance in vacuo in the cold, nor by long heating. Storage of the acid over P_2O_5 for long periods (more than two months) led to its dehydration, which caused an increase of the melting point of the substance to 145° and an increase of the molecular weight.

The trichloromethylphosphinic acid was dibasic; with a solution of $AgNO_3$ it gave a water-insoluble di-silver salt, which had the capacity of decomposing explosively on slight heating (light touch with a heated rod). In an excess of aniline the acid formed the dianiline salt which, being unstable, gradually lost one aniline molecule on storage or on recrystallization, being converted to the monoaniline salt, which also was readily obtained by reaction of the acid with the equivalent quantity of aniline.

This capacity of trichloromethylphosphinic acid to give the dianiline salt, which was noted also for chlorobromomethylphosphinic acid, is explained by the presence of the polyhalogenated methyl radical in these acids. Chloromethylphosphinic and bromomethylphosphinic acids, as we have already noted, even in an excess of aniline, formed only the monoaniline salts. By the reaction of trichloromethylphosphinic acid with diazomethane the dimethyl ester of trichloromethylphosphinic acid, which was a solid crystalline substance with a m. p. of 37°, was obtained quantitatively.

The above-described properties of the esters of trichloromethylphosphinic acid did not agree accurately with those indicated in G. Kamai's works [3, 4, 5, 6].

According to Kamai, the esters of trichloromethylphosphinic acid which he obtained according to the reaction:

$$CCl_4 + P(OR)_3 \rightarrow CCl_3PO(OR)_2 + RCl,$$

on saponification with hydrochloric acid under conditions similar to those which we used, gave not trichloromethylphosphinic, but phosphorous acid, according to the scheme:

$$CCl_3PO(OR)_2 + 2HCl + H_2O \rightarrow 2RCl + 3HCl + (HO)_2P(O)COOH, \quad (HO)_2P(O)COOH \rightarrow CO_2 + P(OH)_3.$$

This circumstance induced us to repeat Kamai's experiment. By careful distillation of the trimethylphosphite and triethylphosphite reaction products with CCl_4, we obtained the methyl and ethyl esters, respectively, which were similar in constants to those which we obtained earlier (see Table).

Saponification of these esters under the conditions which we used (4 hours in an ampoule with 15% HCl at 140-150°) gave trichloromethylphosphinic acid, as did also the saponification of the esters which we obtained earlier.

Thus, Kamai's negative results in his attempts to obtain trichloromethylphosphinic acid can be explained only by the use of an unsuccessful method of separation of the saponification products of the esters. For an additional confirmation of the identity of the esters, obtained by the reactions of $CCl_3PCl_4 + C_2H_5ONO$ and $CCl_4 + P(OC_2H_5)_3$, we planned to carry out their reaction with aniline which, according to Kamai [5], led to the anilide of the dialkylphosphoric acid.

$$CCl_3PO(OR)_2 + C_6H_5NH_2 \rightarrow CCl_3H + C_6H_5NHPO(OR)_2.$$

In attempts to carry out this reaction with the esters obtained by both the first and second scheme, it was noted that no visible reaction of the esters with aniline took place at room temperature. However, after a 2- or 3-hour boiling of the mixture of the components in toluene and after cooling the reaction mixture, in both cases identical acicular crystals of a substance separated, which according to analyses, proved to be not the anilide, but the anilide acid salt of the ester of trichloromethylphosphinic acid $CCl_3PO(OC_2H_5)OH \cdot C_6H_5NH_2$.

Similarly, under the conditions described, the dimethyl ester of trichloromethylphosphinic acid also reacts with aniline, forming the acid salt of the ester $CCl_3PO(OCH_3)OH \cdot C_6H_5NH_2$.

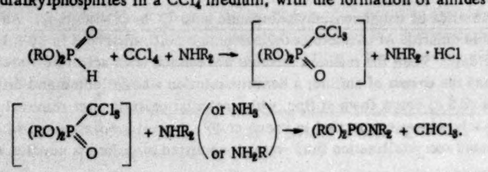
Thus, the reaction between the compounds indicated consists not of the cleavage of the C–P bond in the molecule of the ester of trichloromethylphosphinic acid, but apparently consists of the alkylation of aniline by it.

$$CCl_3PO(OR)_2 + C_6H_5NH_2 \rightarrow CCl_3PO(OR)OH + C_6H_5NHR$$
$$CCl_3PO(OR)OH + C_6H_5NH_2 \rightarrow CCl_3PO(OR)OH \cdot C_6H_5NH_2.$$

Constant	Esters obtained by the new methods		Isolated by us from the products obtained by Kamai's method		Kamai's data	
	methyl	ethyl	methyl	ethyl	methyl	ethyl
boiling point	Crystals 109° (9 mm)	124° (15 mm)	109° (9 mm)	123° (13 mm)	Liquid 122° (12 mm)	122-123° (12 mm)
melting point	37°	–	36-37°	–	–	–
d_0	(50°) 1.4810	(14°) 1.3700	(50°) 1.4830	(14°) 1.3710	(15°) 1.4594	(14°) 1.3664
n_D	(50°) 1.4615	(20°) 1.4615	(50°) 1.4620	(20°) 1.4620	(14°) 1.4580	(14°) 1.4585

Lugovkin and Arbuzov [7] showed the ease of such an alkylation of aromatic amines by the esters of the acids of pentavalent phosphorus (acid chloride of dialkylphosphoric acid).

In a series of works, Todd and Atherton [8] described the phosphorylation reaction of amines, which proceeded by their reaction with dialkylphosphites in a CCl_4 medium, with the formation of amides of dialkylphosphoric acid.



$$(RO)_2P(=O)H + CCl_4 + NHR_2 \rightarrow \left[(RO)_2P(=O)CCl_3\right] + NHR_2 \cdot HCl$$
$$\left[(RO)_2P(=O)CCl_3\right] + NHR_2 \begin{pmatrix}\text{or } NH_3\\ \text{or } NH_2R\end{pmatrix} \rightarrow (RO)_2PONR_2 + CHCl_3.$$

Aniline was also present in a number of investigations of the amines by Todd and Atherton. In not one case did the authors themselves succeed in isolating an intermediate ester of trichloromethylphosphinic acid, arising according to this scheme. Kamai, indicating the property of the esters of trichloromethylphosphinic acid to undergo cleavage by the action of amines (aniline), with the formation of the products described by Todd and Atherton, assumed that his observations confirmed the validity of the above-cited reaction mechanism. At least for aniline, the results of the present investigation, obtained under the conditions described, did not confirm Kamai's data, and placed in doubt the correctness of the scheme of the phosphorylation mechanism of the amines proposed by Todd and Atherton.

EXPERIMENTAL

Chlorination of chloromethyldichlorophosphine. Production of phosphorus trichloromethyltetrachloride. CCl_3PCl_4. Dry chlorine was passed into a solution of 15 g of chloromethyldichlorophosphine in 250 ml of carbon tetrachloride at a temperature of –5-0° until the appearance of the non-fading color of chlorine. Then the temperature in the reaction mixture rose to +30-35°, and the chlorination was continued for 30 minutes more, after which the solvent was removed in vacuo (bath temperature did not exceed 35°). In the residue were colorless, hygroscopic crystals with a m. p. of 125-126° (with decomp.) (in sealed capillary). The yield was quantitative. The substance hydrolyzed very slowly and non-quantitatively (3 chlorine atoms were hydrolyzed). 0.5 N alkali, with boiling, brought about the complete decomposition of the substance.

3.085 mg sub.: 0.480 mg CO_2. 3.560 mg sub.: 0.525 mg CO_2. 0.085 g sub. (in bomb): 20.16 ml 0.1 N $AgNO_3$. 0.3400 g sub.: 16 g benzene: Δt 0.386°. Found %: C 4.24, 4.02; Cl 84.21; P 10.16. M 281. CCl_3PCl_4. Calculated %: C 4.27; Cl 85.08; P 10.65; M 291.5.

Production of the acid dichloride of trichloromethylphosphinic acid – CCl_3POCl_2. 10 g of chloromethyldichlorophosphine was chlorinated in carbon tetrachloride as described above, until the formation of CCl_3PCl_4. Then the excess of chlorine and most of the solvent were driven off in vacuo at +30°, dry SO_2 was passed into the remaining solution (about 30-40 ml), at first in the cold (ice water), and then for 30 minutes at +30°.

The rest of the solvent was removed in vacuo. A dry, colorless substance remained, which consisted of fine crystals which were hygroscopic and which decomposed on storage in the air. The substance had a m. p. of 155°, dissolved well in CCl_4 and in benzene, but dissolved little in cold water. By the action of 0.5 N potassium hydroxide on the substance at room temperature, hydrolysis proceeded readily with the splitting off of 1 chlorine atom, but the hydrolysis did not go to completion (splitting off of 2 chlorine atoms). The chlorine, bound to both the phosphorus and the carbon, was hydrolyzed on heating.

5.320 mg sub.: 1.045 mg CO_2. 5.310 mg sub.: 0.985 mg CO_2. 0.0641 g sub. (in bomb): 13.43 ml 0.1 N $AgNO_3$. 0.110 g sub.: 0.8946 g molybdate. 0.1012 g sub.: 0.8351 g molybdate. 0.4690 g sub.: 16 g benzene: Δt 0.600°. Found %: C 5.35, 5.06; Cl 74.29; P 13.48, 13.64. M 246. CCl_3POCl_2. Calculated %: C 5.08; Cl 75.06; P 13.16; M 236.5.

Production of the monoanilide – $CCl_3PO(Cl)NHC_6H_5$. 3.7 g of aniline was added to 2.3 g of CCl_3POCl_2 in 15 ml of benzene. After 3 hours the acid chloride of aniline was filtered by suction; the rest of the aniline was removed by washing with acidified water. The solvent was removed after drying the benzene solution over sodium sulfate. The oil which remained quickly crystallized (1.5 g). After recrystallization from aqueous alcohol and then from a mixture of hexane with carbon tetrachloride, it consisted of thin prisms with a m. p. of 113-113.5°.

10.42 mg sub.: 7.172 ml 0.02 N $AgNO_3$. 10.20 mg sub.: 7.023 ml 0.02 N $AgNO_3$. 3.910 mg sub.: 0.1695 ml N_2 (22°, 751 mm); 4.893 mg sub.: 0.1998 ml N_2 (22°, 751 mm). 0.1055 g sub.: 16 g benzene: Δt 0.120°. Found %: Cl 48.82, 48.65; N 4.93, 4.55. M 286. $CCl_3PO(Cl)NHC_6H_5$. Calculated %: Cl 48.47; N 4.77, M 293.

Production of the dianilide of trichloromethylphosphinic acid $CCl_3PO(NHC_6H_5)_2$. An excess of aniline (15 g) was added to 5 g of the acid chloride of trichloromethylphosphinic acid, dissolved in 30 ml of benzene, and the mixture was left for three days. Then the reaction mixture was washed with acidified water in order to remove the acid chloride of aniline and the excess of aniline; a benzene solution was collected and dried over sodium sulfate. The almost pure dianilide (2.2 g) came down as fine, white acicular crystals after removal of a portion of the benzene. The remaining solvent was evaporated in vacuo at 40°; the residue was an oil which crystallized after a day (4.5 g). After repeated recrystallization from water it consisted of colorless needles with a m. p. of 172°.

9.495 mg sub.: 4.025 ml 0.02 N $AgNO_3$. 9.615 mg sub.: 4.097 ml 0.02 N $AgNO_3$. 5.337 mg sub.: 0.4070 ml N_2 (21°, 745 mm). 5.285 mg sub.: 0.4000 ml N_2 (21°, 745 mm). 0.2010 g sub.: 16 g benzene: Δt 0.192°. Found %: Cl 30.06, 30.22; N 8.41, 8.43. M 331.5. $CCl_3PO(NHC_6H_5)_2$. Calculated %: Cl 30.47; N 8.02, M 349.5.

Production of the diethyl ester of trichloromethylphosphinic acid $CCl_3PO(OC_2H_5)_2$. 30 ml of ethyl nitrite (2.5-3 fold excess) was condensed in 10 g of CCl_3PCl_4, cooled to –50°, then the cooling was stopped and the mixture was boiled under reflux for 4 hours, with a condenser with brine cooling, the temperature of which rose gradually from –5° to +10°; moreover, the solution grew lighter, depending on the degree of removal of nitrosyl chloride. The reaction was completed when drops of the solution of the aqueous hydrolyzate ceased to precipitate silver from a solution of $AgNO_3$, after which the mixture was repeatedly distilled. 4.5 g of a fraction with a b. p. of 104-105.5° (6 mm), or 124° (15 mm), was collected. It was a colorless, oily liquid with a pleasant fruity odor:

d_0^{14} 1.3700, n_D^{20} 1.4615.

3.780 mg sub.: 3.240 mg CO_2; 1.190 mg H_2O. 5.190 mg sub.: 4.385 mg CO_2; 1.730 mg H_2O. 0.0976 g sub.:* 11.65 ml 0.1 N $AgNO_3$. 0.2020 g sub.: 16 g benzene: Δt 0.260°. Found %: C 23.37, 23.04; H 3.52, 3.72; Cl 42.37. M 248.5. $CCl_3PO(OC_2H_5)_2$. Calculated %: C 23.50; H 3.90; Cl 41.63. M 255.5.

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* A weighed portion was sealed in a tube with 5 ml of C_2H_5OH containing 1 g of dissolved Na, and heated for 2 hours at 150°. Then the contents were boiled in a flask in order to remove the gases, and acidified with HNO_3 and titrated with $AgNO_3$.

Production of trichloromethylphosphinic acid – $CCl_3PO(OH)_2$. 4.5 g of $CCl_3PO(OC_2H_5)_2$, obtained as described above, was heated in an ampoule for 4 hours at 140° with a 5-fold quantity by volume (15 ml) of 15% hydrochloric acid. On cooling, the reaction mixture separated into two layers. The upper layer (about 2 g) consisted of ethyl chloride. The lower layer was evaporated in vacuo on the water bath at 70-80°. The residue crystallized. After a 2-day drying of the crystals in a vacuum-desiccator over P_2O_5, they were recrystallized from benzene (solubility 2 g per 200 ml of boiling benzene) or from carbon tetrachloride (solubility 1 g per 200 ml of boilin CCl_4). The fine needles with a m. p. of 87° were readily soluble in acetone, ether and water.

6.300 mg sub.: 1.300 mg CO_2; 1.280 mg H_2O. 5.390 mg sub.: 1.125 mg CO_2; 1.105 mg H_2O. 14.460 mg sub.: 10.21 ml 0.02 N $AgNO_3$. 11.890 mg sub.: 8.36 ml 0.02 N $AgNO_3$. 0.0256 g sub.: 0.2248 g molybdate. 0.0312 g sub.: 0.2715 g molybdate. 2.215 mg sub.: 1.108 ml CH_4 (0°, 760 mm). 2.710 mg sub.: 1.055 ml CH_4. 0.1524 g sub.: 7.65 ml 0.1 N KOH (by methyl orange) 13.75 ml (by phenolphthalein) 0.1786 g sub.: 9.10 ml 0.1 N KOH (by methyl orange) 16.13 ml (by phenolphthalein) Found %: C 5.63, 5.67; H 2.26, 2.34; Cl 49.88, 50.06; P 14.50, 14.39; active H 1.755, 1.728. Equiv 197, 194 (by methyl orange) 109, 108.5 (by phenolphthalein) $CCl_3PO(OH)_2 \cdot H_2O$. Calculated %: C 5.52; H 1.83; Cl 49.08; P 14.28; active H 1.83, Equiv. 217.5, 108.6.

Thus, the crystals with a m. p. of 87° were the monohydrate of trichloromethylphosphinic acid. Heating of the substance for 2 hours at 100° led to no loss of the water of crystallization. The acid dehydrated on standing over P_2O_5 in a vacuum-desiccator for 2-3 months, which led to an increase of the melting point of the sample to 145°, to the loss of active hydrogen, and to an increase of the molecular weight (340 in acetophenone).

Production of the silver salt of trichloromethylphosphinic acid – $CCl_3PO(OAg)_2$. An excess of a concentrated solution of $AgNO_3$ was added to 0.5 g of trichloromethylphosphinic acid (m. p. 87°) dissolved in 5 ml of water. A finely-crystalline precipitate which was difficultly soluble in water, but soluble in dilute HNO_3, came down immediately. The precipitate was filtered off, washed with alcohol and ether, and dried. In the dry form the substance exploded on touching a slightly heated rod to it. The yield was quantitative.

0.1117 g sub.: 5.30 ml 0.1 N NH_4CNS. 0.0775 g sub.: 3.75 ml 0.1 N NH_4CNS. Found %: Ag 51.19, 52.19. $CCl_3PO(OAg)_2$. Calculated %: Ag 52.21.

Production of the dianiline salt of trichloromethylphosphinic acid $CCl_3PO(OH)_2 \cdot 2C_6H_5NH_2$. An excess of aniline (1 g) was added to a suspension of 0.5 g of the trichloromethylphosphinic acid with a m. p. of 87° in 15 ml of benzene. After two days the insoluble dianiline salt was filtered off and recrystallized from alcohol containing 2% aniline. The fine needles were kept in a desiccator over aniline. The substance did not melt up to 220°, but decomposed. The yield was quantitative.

3.275 mg sub.: 0.2280 ml N_2 (28°, 740 mm). 3.010 mg sub.: 0.2120 ml N_2 (28°, 740 mm). 10.100 mg sub.: 3.950 ml 0.02 N $AgNO_3$. 11.300 mg sub.: 4.400 ml 0.02 N $AgNO_3$. Found %: N 7.80, 7.70; Cl 27.77, 27.65. $CCl_3PO(OH_2) \cdot 2C_6H_5NH_2$. Calculated %: N 7.27; Cl 27.66.

Production of the monoaniline salt of trichloromethylphosphinic acid – $CCl_3PO(OH)_2 \cdot C_6H_5NH_2$. A mixture of 50 ml of benzene, 2 g of trichloromethylphosphinic acid and 0.93 g of aniline was left for two days. Then the precipitate (2.9 g) was separated and recrystallized from acetic acid or from water. It consisted of flaky crystals which did not melt up to 220°.

4.140 mg sub.: 0.1860 ml N_2 (22°, 744 mm). 5.105 mg sub.: 0.2350 ml N_2 (22°, 744 mm). Found %: N 5.22, 5.09. $CCl_3PO(OH)_2 \cdot C_6H_5NH_2$. Calculated %: N 4.78.

Production of the dimethyl ester of trichloromethylphosphinic acid – $CCl_3PO(OCH_3)_2$. A solution of 3.2 g (3 moles) of diazomethane in 150 ml of ether was added to a solution of 5 g (1 M) of trichloromethylphosphinic acid in 50 ml of ether at a temperature of –10°. After removal of the ether about 5 g of a residue was obtained, which distilled almost completely at 110-113° (9 mm). Pure dimethyl ester with a b. p. of 109° (9 mm) and a m. p. +37° was obtained by repeated distillation.

d_0^{50} 1.4810, n_D^{50} 1.4615.

0.1024 mg sub.: 13.35 ml 0.1 N $AgNO_3$. 0.0886 g sub.: 46.10 ml 0.1N $Na_2S_2O_3$. 0.0707 g sub.: 36.77 ml 0.1 N $Na_2S_2O_3$. 0.4810 g sub.: 16 g benzene: Δt 0.665°. Found %: Cl 46.23; OCH_3 26.90, 28.89. M 232. $CCl_3PO(OCH_3)_2$. Calculated %: Cl 46.81; OCH_3 27.10. M 227.5.

Production of the dimethyl ester of trichloromethylphosphinic acid by Kamai's method. The reaction was carried out exactly according to the description [3]. A fraction with a b. p. of 109° (9 mm) and a m. p. of 37° was separated by a precise distillation. The constants of the substance – d_0^{50} 1.4830 and n_D^{50} 1.4620 – agreed exactly with those obtained for the ester formed by the reaction of trichloromethylphosphinic acid with diazomethane.

Production of the diethyl ester of trichloromethylphosphinic acid by Kamai's method. The reaction was carried out exactly according to the description [3]. After a precise distillation a substance with a b. p. of 122-123° (13 mm), d_0^{14} 1.3710, n_D^{20} 1.4620 was separated, i. e., a substance with constants which agreed with those of the diethyl ester which we obtained earlier and which differed somewhat from that described by Kamai [b. p. 122-123° (12 mm), d_0^{14} 1.3664, n_D^{14} 1.4585].

Saponification of the diethyl ester of trichloromethylphosphinic acid obtained by Kamai's method. 4.5 g of the diethyl ester of trichloromethylphosphinic acid, obtained by Kamai's method, was saponified with 15 ml of 15% hydrochloric acid under conditions which we employed for the production of trichloromethylphosphinic acid. After removal of the aqueous solution in vacuo, 4.1 g of a crystalline substance remained, which after drying and recrystallization from benzene had a m. p. of 87°, and proved to be identical with the trichloromethylphosphinic acid obtained as described earlier (sample of a mixture of the indicated acids gave no depression on melting).

Reaction of the diethyl ester of trichloromethylphosphinic acid with aniline. 1 g of the diethyl ester of trichloromethylphosphinic acid (obtained by any of the methods described above) was mixed with 3 ml of aniline and 30 ml of toluene and boiled for 2 hours. Crystals precipitated from the reaction mixture, on cooling. On the next day they were filtered off (1.2 g) and washed with benzene. The reaction took place identically esters. Fine needles with a m. p. of 174-176° (with decomp.) were obtained.

5.170 mg sub.: 6.270 mg CO_2; 2.050 mg H_2O. 16.910 mg sub.: 3.116 ml 0.05 N $AgNO_3$. 4.599 mg sub.: 0.2060 ml N_2 (23°, 735 mm). 4.490 mg sub.: 0.1990 ml N_2 (23°, 735 mm). 0.0588 g sub.: 10.71 ml 0.1 N $Na_2S_2O_3$. 0.0722 g sub.: 13.15 ml 0.1 N $Na_2S_2O_3$. 0.1015 g sub.: 3.20 ml 0.1 N KOH (by phenolphthalein) 0.1490 g sub.: 4.73 ml 0.1 N KOH (by phenolphthalein). Found %: C 33.08; H 4.43; Cl 32.67; N 4.99, 4.36; OC_2H_5 13.67, 14.04. Equiv. 317, 320.5. $CCl_3PO(OC_2H_5)OH \cdot C_6H_5NH_2$. Calculated %: C 33.67; H 4.05; Cl 33.23; N 4.93; OC_2H_5 13.67. Equiv. 314.0.

Reaction of the dimethyl ester of trichloromethylphosphinic acid with aniline. 1 g of the dimethyl ester of trichloromethylphosphinic acid (obtained by any of the methods described above) was mixed with 3 ml of aniline and 30 ml of toluene and boiled for 2 hours. On cooling, crystals – colorless needles – separated from the reaction mixture. On the next day they were separated (1 g) and washed with benzene. The product obtained was similar to that described above and had a m. p. of 172° (with decomp.)

3.813 mg sub.: 4.355 mg CO_2; 1.091 mg H_2O. 11.050 mg sub.: 5.340 ml 0.02 N $AgNO_3$. 4.720 mg sub.: 0.1890 ml N_2 (25°, 761 mm). 4.775 mg sub.: 0.2030 ml N_2 (25°, 761 mm). 0.0630 g sub.: 12.0 ml 0.1 N $Na_2S_2O_3$. 0.0396 g sub.: 7.45 ml 0.1 N $Na_2S_2O_3$. 0.1374 g sub.: 4.60 ml 0.1 N KOH (by phenolphthalein). 0.0949 g sub.: 3.16 ml 0.1 N KOH (by phenolphthalein). Found %: C 31.15; H 3.20; Cl 34.31; N 4.65, 4.89; OCH_3 9.85, 9.74. Equiv. 300, 300. $CCl_3PO(OCH_3)OH \cdot C_6H_5NH_2$. Calculated %: C 31.32; H 3.25; Cl 34.75; N 4.56; OCH_3 10.13. Equiv. 306.5.

Production of phosphorus dichloromethyltetrachloride. The calculated quantity of a solution of chlorine in CCl_4 was slowly introduced dropwise into 5 g of chloromethyldichlorophosphine dissolved in 150 mg of carbon tetrachloride, with cooling (ice and salt). The chlorine color in the reaction mixture disappeared rapidly. On addition of the total quantity of chlorine, most of the solvent was removed in vacuo, and a finely-crystalline, white, hygroscopic phosphorus dichloromethyltetrachloride precipitate, which deliquesced in the air, came down.

0.1770 g sub.: (in 25 ml 0.5 N KOH): 27.30 ml 0.1 N $AgNO_3$. 0.1520 g sub.: (in 25 ml 0.5 N KOH): 23.50 ml 0.1 N $AgNO_3$. Found %: Cl hyd. 54.76, 54.89. CCl_2HPCl_4. Calculated %: Cl hyd. 55.25.

Production of dichloromethylphosphinic acid – $CCl_2HPO(OH)_2$. 1 g of CCl_2HPCl_4 was hydrolyzed by 3 ml of warm (40°) water. After removal of the excess water in vacuo, and after drying the substance over P_2O_5 in a desiccator, it consisted of course, acicular crystals, which rapidly moistened in the air, and had a m. p. of 53°. Its m. p. was 115° after repeated recrystallization from benzene.

5.065 mg sub.: 1.272 mg CO_2; 0.585 mg H_2O. 4.090 mg sub.: 1.056 mg CO_2; 0.477 mg H_2O. 10.285 mg sub.: 6.295 ml 0.02 N $AgNO_3$. 5.115 mg sub.: 3.082 ml 0.02 N $AgNO_3$. Found %: C 6.85, 5.98; H 1.29, 1.30; Cl 43.43, 42.68. $CCl_2HPO(OH)_2$. Calculated %: C 7.27; H 1.80; Cl 43.03.

Bromination of chloromethyldichlorophosphine. Production of chlorobromomethylphosphinic acid – $ClBrCHPO(OH)_2$. An excess of bromine (10 g) in 25 ml of CCl_4 was introduced dropwise, with stirring, into a cooled (ice and salt) solution of 5 g of $ClCH_2PCl_2$ in 26 ml of CCl_4. Then the bath temperature rose to 50° and was maintained so for 2 hours, after which the solvent was removed in vacuo, and the residue was decomposed with water. The substance crystallized on standing over P_2O_5 and KOH in a vacuum-desiccator.

The crystalline substance (3.5 g) was pressed on a dry porous plate. The product was extremely hygroscopic and immediately deliquesced in the air. The aniline salt was obtained by pouring together a benzene solution of the acid with an excess of aniline. After its recrystallization from alcohol, the fine needles with a m. p. of 180-185° (with decomp.) contained chlorine and bromine.

4.805 mg sub.: 0.2860 ml N_2 (30°, 746 mm). 3.770 mg sub.: 0.2270 ml N_2 (30°, 746 mm). Found %: N 6.59, 6.69; $ClBrCHPO(OH)_2 \cdot 2C_6H_5NH_2$. Calculated %: N 7.08.

SUMMARY

1. The action of chlorine and bromine on chloromethyldichlorophosphine was investigated, and it was found that di- and trihalomethylphosphinic derivatives formed in this way. Dichloromethyl-, chlorobromomethyl-, and trichloromethylphosphinic acids were isolated and characterized (salts, ester, and acid halides).

2. The literature data notwithstanding, it was found that the esters of trichloromethylphosphinic acid can be: a) normally converted to trichloromethylphosphinic acid by saponification, and b) by reaction with aniline converted to the corresponding acid esters in this reaction no cleavage of the C–P bond was observed.

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INVESTIGATION OF BASIC FERRIC SALTS

B. A. Ryazanov

The question of basic salts of ferric oxide is far from having been clarified up to the present time. The kinetics of hydrolysis for ferric salts, and the formation conditions of basic salts have not been adequately studied. Certain of the more important properties of soluble basic salts of ferric oxide, and their behavior, have been studied mainly by Soviet investigators [1-3]. A study of basic salt precipitates resulting from the sulfate of ferric oxide with various alkalies has led to a considerable number of compounds with varied ratio between ferric oxide and sulfur trioxide [4-5]. There exists no unanimous point of view concerning the nature of such products obtained when alkali is reacted with ferric salts, and it is not possible to draw any definite conclusions to the composition and number of basic salts of ferric oxide.

To investigate the interaction of ferric oxide salts with alkali, the author used a physico-chemical method of analysis which was developed by Kurnakov and his school.

EXPERIMENTAL

Study of the sulfates of ferric oxide basic salts was carried out by the isothermal method. To carry out each experiment at 25°, the appropriate volumes of $Fe_2(SO_4)_3$ and KOH were taken.

0.0409 m.-eq. of H_2SO_4 was taken per 1 m.-eq. of $Fe_2(SO_4)_3$ in the initial solution of ferric salt. The pH of the solution was equal to 1.4. Standard flasks were used for work on solubility determinations, equipped with stirrer and oil seal to prevent absorption of carbon dioxide from the air. The flasks were placed in a water thermostat at 25°. Temperature variation did not exceed ±0.1°. Accurately measured volumes of $Fe_2(SO_4)_3$ were poured into the flasks, stirring begun, and finally the corresponding volumes of potassium hydroxide solution added drop by drop from a burette. Continuous 24-hour stirring was carried out, to the establishment of chemical equilibrium between the liquid and solid phases, determination of which equilibrium was carried out by coincidence of analytical results for ferric ions, or sulfate radical, in the last samples of transparent supernatant over the precipitate. After attainment of equilibrium, stirring was terminated and chemical analysis carried out according to the Schreinemaker residue method. The amounts of ferric oxide, potassium and sulfate ions, were determined. Trivalent iron was determined iodometrically, sulfate ion gravimetrically, according to the method developed by Nikitina and Babaeva [6], quantitative determination of potassium ions being carried out as sulfate by the gravimetric procedure. The pH of the solutions was determined by glass electrode. For determination of the composition of solid phases, portions of the complex quaternary system $K_2O-Fe_2O_3-SO_3-H_2O$ were investigated. Experiments carried out belong to the projection ray study of characteristic points for composition of the system on the plane for $KOH-Fe(OH)_3-H_2SO_4$.

The portion of indicated quaternary systems studied can be graphically represented by a tetrahedron, at one of whose corners is the constituent water, and at the base of which tetrahedron three of the components in hydrated form: KOH, H_2SO_4, $Fe(OH)_3$.

There is given in Fig. 1 the construction of such a tetrahedral space diagram in the form of an equilateral triangle. From the appearance of the diagram constructed the chemical nature of the substances formed in the system can be evaluated. In Fig. 1 the apices of the triangle correspond to pure components, and the sides to the systems having two components. The compositions of the initial mixtures for liquid and solid phases for the established equilibrium (Fig. 1) are expressed in milliequivalent percentages for the amounts of iron, potassium and sulfate ion.

From the diagram (Fig. 1) the following deductions can be made.

1. In that section of the diagram which is rich in iron ions (experiments 1-7) where for the weight quantity of potassium hydroxide taken, there was used 86.7 - 62.5 m-eq. % of $Fe_2(SO_4)_3$, the lines converge at one spot on the diagram. It is known that if points are present on the lines which determine the composition of the solid phase, and

TABLE 1

Compositions of the initial compounds taken for experiment

Experiment No.	Percent milliequivalent		Milliequivalents available for 40 ml of initial mixture.			
	Iron•	KOH••	K^+	Fe^{+++}	SO_4^{--}	OH^-
1	90.9	9.1	3.446	34.50	35.91	2.036
2	86.7	13.3	6.260	40.73	42.39	4.60
3	82.1	17.9	6.67	30.67	31.92	5.42
4	77.5	22.5	10.43	35.94	37.41	8.96
5	72.1	27.9	10.38	26.83	27.93	9.28
6	68.1	31.9	11.68	24.92	25.94	10.66
7	62.5	37.5	13.78	23.00	23.94	12.84
8	58.4	41.6	15.01	21.08	21.95	14.14
9	52.6	47.4	17.29	19.17	19.95	16.51
10	43.4	56.6	20.02	15.33	15.96	19.39
11	32.2	67.8	24.21	11.50	11.97	23.74
12	22.3	77.7	26.69	7.67	7.98	26.38
13	11.3	88.7	30.02	3.833	3.990	29.86

if these lines within the diagram intersect, then their point of intersection characterizes the solid phase as a chemical compound of definite composition. For 1 mole of $Fe_2(SO_4)_3$, there is assigned for this intersection point on the diagram 2.5 moles of $Fe(OH)_3$ and 0.75 mole of K_2SO_4. Hence the solid phase found should represent a basic salt of ferric oxide of the composition:

$$4Fe_2(SO_4)_3 \cdot 10Fe(OH)_3 \cdot 3K_2SO_4.$$

The simplest formula for this salt is

$$3Fe_2O_3 \cdot 5SO_3 \cdot K_2O \cdot 5H_2O \text{ or } 4FeOHSO_4 \cdot 2Fe(OH)_3 \cdot K_2SO_4.$$

There is given in Table 2 the composition of precipitates, calculated according to the data from chemical analysis.

For the indicated experiments (1-7), at pH 1.8, there was formed a fine cyrstalline anisotropic, light-yellow precipitate. Chemical analysis of these cyrstalline precipitates confirmed the chemical composition of the solid phase found by the graphical method according to the diagram. In experiment 7, a crystalline precipitate was formed with utilization of the entire amount of iron contained in the original mixture. In experiment 1 with a ferric ion content of 90.9 m-eq. %, traces of crystalline precipitate were obtained, despite continuous around-the-clock stirring for 350 hours.

TABLE 2

Chemical analysis of the precipitate

Experiment No.	No. of Fe^{+++} ions in the initial mixture (in m-eq. %)	No. of milliequivalents contained in 1 g. of precipitate			Chemical composition of the solid phase.
		K^+	Fe^{+++}	SO_4^{--}	
2	86.7	1.320	12.84	6.980	$Fe_2(SO_4)_3 \cdot 2.5Fe(OH)_3 \cdot 0.7K_2SO_4$
3	82.1	1.622	14.984	8.107	$Fe_2(SO_4)_3 \cdot 2.6Fe(OH)_3 \cdot 0.75K_2SO_4$
4	77.5	1.560	15.19	8.260	$Fe_2(SO_4)_3 \cdot 2.5Fe(OH)_3 \cdot 0.7K_2SO_4$
5	72.1	1.650	13.14	7.600	$Fe_2(SO_4)_3 \cdot 2.4Fe(OH)_3 \cdot 0.8K_2SO_4$
6	68.1	1.200	9.830	5.600	$Fe_2(SO_4)_3 \cdot 2.5Fe(OH)_3 \cdot 0.8K_2SO_4$
7	62.5	1.048	9.750	5.250	$Fe_2(SO_4)_3 \cdot 2.6Fe(OH)_3 \cdot 0.75K_2SO_4$

The line in this experiment passes through a point which determines the composition of the solid phase in experiment 2.

• 0.9583 N $Fe_2(SO_4)_3$.

•• 0.8340 or 0.8614 N KOH.

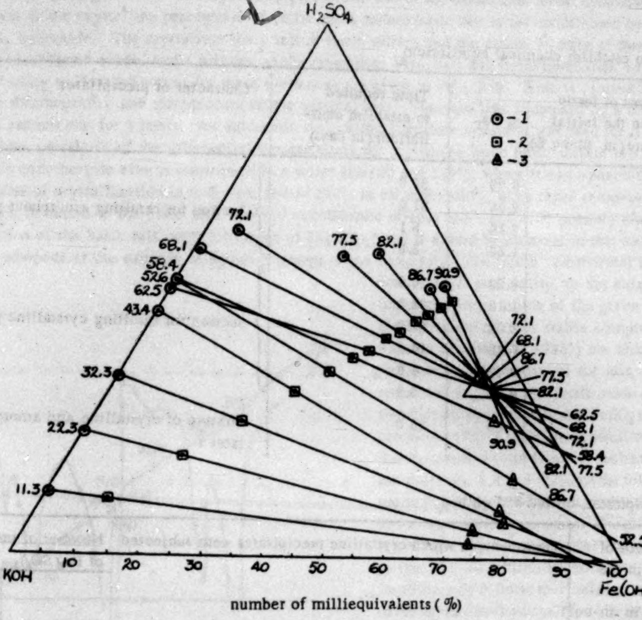

Fig. 1. Structure of the tetrahedron diagram for the system $K_2O-Fe_2O_3-SO_3-H_2O$.

1) Composition of the liquid phase, 2) composition of the initial mixture, 3) composition of the solid phase.

2. The directions of the lines in that section of the diagram with a content of 58.4 - 52.6 m-eq.% of ferric ions attest to the fact that at pH 2.5 - 2.67 a mixture of crystalline salt and ferric oxide hydrate results (compositions of the liquid phases in these experiments approximating the composition of pure potassium sulfate solutions.).

3. The lines in the section containing 43.4 - 11.3 m-eq. % of ferric ions (experiments 10-13) converge at a point which is close to the point for pure ferric oxide hydrate. The amorphous precipitates, red-brown in color, obtained in experiments at pH 11.0 - 13.45, should thus represent adsorption products of alkali and potassium sulfate with the hydrate of ferric oxide.

4. It can be seen from the diagram that the smallest value for ratio of segment length on the line from the point for total composition of initial mixture to the point of composition for residue (a_2), and from the point of composition for initial mixture to the points of composition of liquid phase (a_1), corresponds to experiments 5 and 6 (0.49); thus, to obtain the highest yield of basic crystalline salts, there should be taken such amounts of $Fe_2(SO_4)_3$ and KOH that there is available 28-32 m-eq. of alkali in the initial mixture for each 72-68 m-eq. of iron salt.

In determining specific relationships for the ratio a_2/a_1, time is taken to establish chemical equilibrium between liquid and solid phases.

It can be seen from Table 3 that for the section of resulting cyrstalline and amorphous precipitates, chemical equilibrium very slowly becomes established in those experiments, where the smallest amounts of precipitates resulted (31-34 days); especially slowly established was the equilibrium in experiment 8, in which a mixture of crystalline and amorphous precipitates was forming (86 days). A series of investigations was carried out with the crystalline precipitates. They were boiled in the mother liquor and with water in an apparatus equipped with reflux condenser. Following each operation (Table 4), potassium ions were found in the wash waters only for experiment 8.

TABLE 3
Time required to establish chemical equilibrium

Experiment No.	Content of ferric ions in the initial mixture (in m-eq.%)	$a_2 : a_1$	Time required to establish equilibrium (in days)	Character of precipitates
13	11.3	6.29	31.0	Section for resulting amorphous precipitates
12	22.3	2.98	31.0	
11	32.2	2.16	5.1	
10	43.4	1.50	5.0	
2	86.7	4.29	34.0	Section for resulting cyrstalline precipitates
3	82.1	1.18	32.5	
4	77.5	1.02	31.0	
5	72.1	0.49	14.6	
6	68.1	0.49	4.8	
7	62.5	0.60	5.3	
8	58.4	0.80	86.0	Mixture of crystalline and amorphous precipitates

TABLE 4
Crystalline precipitates, boiled and washed

Experiment No.	Content of ions in the initial mixture (in m-eq. %)	Treatments to which crystalline precipitates were subjected	Number of moles per 1 mole of $Fe_2(SO_4)_3$	
			$Fe(OH)_3$	K_2SO_4
4	77.5	Precipitate not washed with water	2.5	0.7
4	77.5	Precipitate washed with water to disappearance of reaction for SO_4^{--} ion	2.5	0.8
4	77.5	Precipitate washed twice with water in apparatus equipped with reflux, for 18 and 10 hours, and washed with water to disappearance of SO_4^{--} test.	3	0.8
5	72.1	Precipitate not washed with water	2.42	0.8
5	72.1	Precipitate boiled 2 hours in mother liquor, then 1 hour with water, and washed with water to disappearance of SO_4^{--} reaction	2.94	0.82
6	68.1	Precipitate not washed with water	2.5	0.8
6	68.1	Precipitate washed with water to disappearance of SO_4^{--} reaction	2.5	0.8
6	68.1	Precipitate was boiled for 2 hours in mother liquor, and then for 1 hour with water, washed with water to disappearance of SO_4^{--} reaction	2.95	0.8
8	58.4	Precipitate not washed with water	5.15	1.36
8	58.4	Precipitate boiled for 18 hours in mother liquor and then twice with water for 3 and 6 hours, and washed with water to disappearance of reaction for SO_4^{--} and K^+	7.3	0.9

The following deductions can be made from Table 4:

1) chemical composition of crystalline precipitate washed with water remains unchanged, 2) crystalline precipitate

begins to hydrolyze upon boiling with water, the potassium sulfate not washing out, 3) in experiment 8, the precipitate representing a mechanical mixture of crystalline basic salt and iron hydroxide, hydrolyzes to a considerable extent, and in this case, washing out of potassium sulfate is observed. In all probability, in forming this reaction, potassium sulfate is adsorbed by ferric hydroxide. X-ray photographs of the crystalline precipitate and of the crystalline ferric hydroxide have demonstrated that the form of the crystalline precipitate of ferric oxide sulfate basic salt is not conditioned by the crystalline form of the ferric hydroxide. The crystalline basic salt of ferric sulfate and the crystal hydrate of ferric sulfate, the amorphous hydrate of ferric oxide, and a mixture of the crystalline basic salt and ferric hydroxide, have been investigated thermographically.* Heating curves for these substances are given in Figs. 2-5. Time is plotted along the horizontal axis on the thermograms, and temperature on the vertical axis. The zero line is marked by a broken line. Observations were carried out for 3 hours. An automatic registering Kurnakov apparatus was used for recording of temperature and time. Analysis of the differential heating curve for crystalline basic ferric sulfate salt (Fig. 2) indicates that the first two endothermic effects correspond to a water loss (90 and 170°), where it can apparently be assumed that at 90° the water of crystallization is removed, and at 170°, in all probability, more rapid removal begins of the water which is more closely bound to the basic salt. A third endothermic effect (365° and 410°) possibly characterizes a partial decomposition of the basic salt, with formation of $Fe_2(SO_4)_3$, and it should be assumed in this case that at 410° water formation proceeds at the expense of hydroxyl groups of the basic salt. The fourth exothermal effect (510°) corresponds, in all probability, to the existence of a regrouping of the atoms inside of the given substance, and to the formation of more stable compounds. The last two thermal effects (710°-775°) are characterized by more profound decomposition of the salt; here is possibly decomposition of $Fe_2(SO_4)_3$ into ferric oxide and SO_3. We might mention that the decomposition of $FeSO_4$ into ferrous oxide and SO_3 proceeds at 725° [7]. Without dwelling upon analysis of other thermograms, a comparison of the heating curves for three substances (Figs. 2,3 and 4) allows the following deductions: there are no $Fe_2(SO_4)_3$ and $Fe(OH)_3$ as individual chemical compounds in the crystalline precipitate. The general outline of the heating curve in Fig. 5 indicates that the precipitate obtained in Experiment 8 is not an individual substance (diffuseness of the planes, insufficiently definite thermal breaks). Upon drying 5.0098 g of the crystalline basic salt for 126 hours at 100°, 0.476 g of water was lost; it did failed to reach constant weight. For this amount of water, recalculating for 1 mole of $4FeOHSO_4 \cdot 2Fe(OH)_3 \cdot K_2SO_4$ gives 5.594 moles of water (Fig. 6).

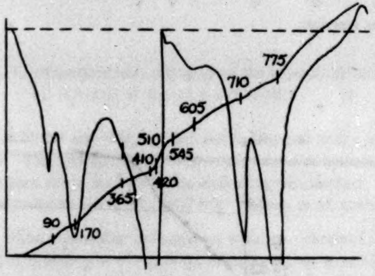

Fig. 2. Curve for the crystalline basic ferric sulfate salt on heating.

If we assumed that the process did not go to completion, then a hypothesis can be made that 6 molecules of crystallization water enter into the composition of 1 molecule of the indicated salt. Thus, this latter experiment, and the heating curves indicated, suggest that the crystalline basic salt is a crystalline hydrate, and hydroxyl groups should enter into the composition of this salt. It should be mentioned that upon investigating a portion of the complex quaternary system $K_2O-Fe_2O_3-SO_3-H_2O$, the hydrated oxides were unaffected. The diagram (Fig. 1) gives a picture of the quantitative relationships of all components except water. The amount of water in the system was not determined every time. Crystalline precipitates of the basic ferric salt are insoluble in water and poorly soluble in hydrochloric acid. 21 ml. of 1.479 N HCl is needed to dissolve 0.0705 g of crystalline basic salt precipitate at room temperature.

In another experiment, complete dissolution of the precipitate was observed only at 100° after addition of 10 ml of 1.479 N HCl to 0.1051 g of the crystalline basic salt. In Fig. 7 a potentiometric curve for titration of 0.1160 g of this salt at 74° is shown. Results of the potentiometric titration indicated that interaction of hydrochloric acid with the basic groups of the salt proceeds with extreme slowness. Such phenomenon, in all probability, is explainable by the fact that the ferric ions in the basic salt are bound quite securely with the hydroxyl ions of oxygen. If there be taken into account the investigations of structure for the polymeric monohydrate $(FeOOH)_4$ [8,10], the polynucleic chain of complexes for basic salts of chromium, and the results of the author's investigations, it can then be considered that the polynucleic stable complex ion enters into the composition of the basic crystalline salt. Thus, the salt can have the structure $K_2^+[Fe_6^{+++}(OH)_{10}^-(SO_4)_5^{--}]^{--}$. If the coordination number for iron is assumed to be 6, and that

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* The investigation was carried out in the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR with the generous participation of L. G. Berg, to whom we express our sincere thanks.

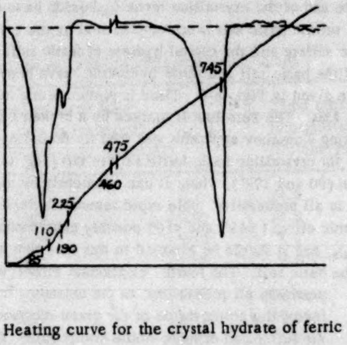


Fig. 3. Heating curve for the crystal hydrate of ferric sulfate.

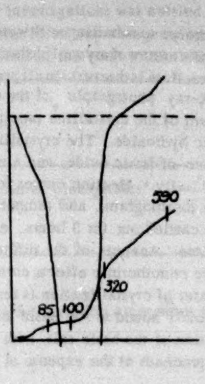


Fig. 4. Heating curve for amorphous ferric hydroxide.

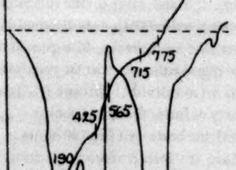


Fig. 5. Heating curve for the mixture of crystalline basic salt and ferric hydroxide.

the OH^- and SO_4^{--} groups are maximally utilized for occupation of spaces in the coordination spheres of the iron atoms, then the crystallohydrate structure for the complex salt can be presented as follows:

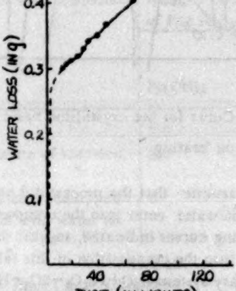
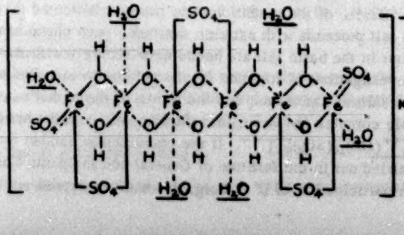


Fig. 6. Water loss upon drying the basic crystalline ferric sulfate salt.



The additional 6 water molecules, not accounted for in the simplest formula, are underlined. A hypothesis can be made that these water molecules were indeed split off upon drying the basic salt at 100° (Fig. 6); however, water evolves from the hydroxyl groups at higher temperatures (as reflected in the thermograms). If there be taken into consideration the fact that the drying process for the precipitate at 100° is not complete, then the 5.6 molecules of water found in this experiment, which are split off at 100°, gives good agreement with the theoretical calculation. Proceeding from the quoted structure for the complex basic double crystalline salt of ferric sulfate,

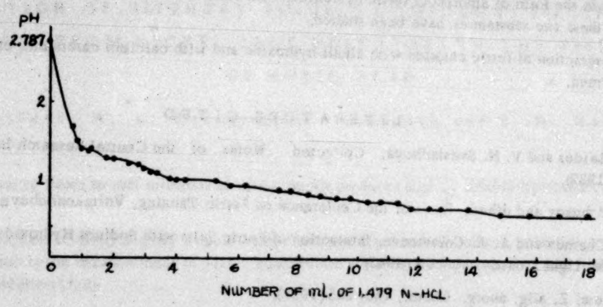


Fig. 7. Potentiometric titration of the crystalline basic salt of ferric sulfate
1. Number of ml. of 1.479 N-HCl

the difficult solubility of this salt in mineral acid can be explained, justifying results of the potentiometric titration. The interaction of hydronium ions with hydroxyl ions, which enter into the composition of the polynuclear complex ferric ion, proceeds with extreme slowness. It is known from the literature [11,12] that the crystalline salt of aluminumsulfate $(Al_2O_3H)_2^+ SO_4^{--}$ reacts in an analogously slow manner.

Fine crystalline precipitates were also obtained by interaction of ferric sulfate with calcium carbonate. Data on the interaction of $Fe_2(SO_4)_3$ with NaOH are given in Table 5. For the initial mixtures of 62.5 and 72.1 m-eq.% of ferric sulfate, 37.5 and 27.9 m-eq. % of sodium hydroxide were taken. Round-the-clock stirring was carried on for 25 days. After termination of the experiment, the resulting amorphous brown-colored precipitates were filtered off and washed with water to the disappearance of reactions for the ions of sulfate and potassium in the wash water.

TABLE 5
Interaction of $Fe_2(SO_4)_3$ with NaOH

Experiment No.	Composition of initial mixture (in		Batch of precipitate taken for analysis (in g)	No. of milliequivalents in 1 g of precipitate		No. of moles of $Fe(OH)_3$ available per 1 mole of $Fe_2(SO_4)_3$ in the precipitate	No. of milliequivalents of sodium ions in the precipitate
	$Fe_2(SO_4)_3$	NaOH		$Fe_2(SO_4)_3$	$Fe(OH)_3$		
1	160	95.80	1.5271	0.907	4.769	10.60	None
2	160	61.94	1.4527	0.976	5.264	10.79	None

It can be seen in Table 5 that the sodium ions do not enter into the composition of the obtained amorphous precipitates, in contrast to similar experiments on the interaction of $Fe_2(SO_4)_3$ with potassium hydroxide. Thus, variable behavior of the $Fe_2(SO_4)_3$ solutions when acted upon by alkali (NaOH, KOH) is conditioned by selection of the alkaline cation. used. Formation of crystallization precipitates was not observed upon interaction of ferric chloride with potassium hydroxide, sodium hydroxide or calcium carbonate.

SUMMARY

As a result of the investigations conducted on basic salts of ferric sulfate, variable behavior of $Fe_2(SO_4)_3$ solutions when acted upon by sodium hydroxide potassium hydroxide has been demonstrated.

1. Precipitates resulting by interaction with sodium hydroxide are amorphous and do not contain sodium sulfate.

2. Precipitates obtained by interaction of $Fe_2(SO_4)_3$ with potassium hydroxide are finely crystalline and contain potassium sulfate in chemically-bound state. They are in the form of a basic salt, possessing the simple formula $4FeOHSO_4 \cdot 2Fe(OH)_3 \cdot K_2SO_4$. It has been demonstrated that the salt in question is a crystalline hydrate and contains a stable, polynuclear complex ion, the structure of which can be represented as $K_2^{+}[Fe_6^{3+}(OH)_{10}^{-}(SO_4)_5^{-}(H_2O)_6]^{--}$.

3. The range of concentration of initial substances wherein the precipitates formed are either the crystalline basic salt or are in the form of amorphous ferric hydroxide, with adsorbed alkali and adsorbed potassium sulfate, or are mixtures of these two substances, have been studied.

4. Upon interaction of ferric chloride with alkali hydroxide and with calcium carbonate, crystalline precipitates are not formed.

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COMPOSITION OF SLIGHTLY SOLUBLE COMPOUNDS PRECIPITATED BY BASES FROM NICKEL SALT SOLUTIONS IN THE PRESENCE OF BORIC ACID

V. L. Kheifets, A. L. Rotinyan, E. S. Kozich and E. N. Kalnina

The addition of bases to salt solutions of many metals produces slightly soluble hydroxides or more complex compounds.

The composition of these slightly soluble compounds and the standard isobaric potentials at which they form may be computed by the measurement of pH (in equilibrium with the solid phase), as a function of the activity of metal salts in solution [1,2].

Complex slightly soluble compounds may be formed from a metal hydrate and the salt of the same metal ($x[\mathrm{Me}_b\mathrm{A}_d]\cdot y[\mathrm{Me}(\mathrm{OH})_n]$), or may contain molecules of foreign compounds (if the latter are present in the solution.).

Obviously, only the first type of slightly soluble compounds may be formed in pure sulfate solutions: their compositions and standard isobaric potentials have been computed in accordance with the general formula:

$$\mathrm{pH} = \frac{\Delta Z^0_{\text{basic}}}{2.3nyRT} - \frac{y + bx + dx}{ny}\log a_{\pm} - \frac{1}{ny}\log\frac{b(y + bx)\,d^{dx}}{\left(\frac{b}{b^{b+d}}\frac{d}{d^{b+d}}\right)^{y + bx + dx}} - \log K_W. \qquad (1)$$

where $\Delta Z^0_{\text{basic}}$ is the standard isobaric potential at which the basic salt begins to form, $a_{\pm}$ is the activity of the metal salt in solution, and K_W is the ion product of the water.

Study of the formation of slightly soluble compounds consisting of metal hydrates and molecules of foreign substances in solutions is also of interest, however.

Rotinyan and Zeldes [3,4] directed attention, a few years ago, to the fact that the addition of boric acid to nickel salt solutions resulted, upon titration with alkali, in the reduction of pH at the beginning of the formation of the solid phase.

At that time no explanation was found for this phenomenon, but after Keshan and his associates [5] discovered the existence of an entire series of slightly soluble metal borates, it became possible to relate the reduction in pH at the beginning of the appearance of the solid phase to the formation of boron-nickel compounds of lower solubility than that of pure nickel hydroxide. Thereupon it was decided to subject the problem of boron-nickel compound formation to more detailed investigation.

The foregoing certainly contradicts the very widespread opinion which holds the role of boric acid in a nickel electrolyte to be limited merely to the buffering properties of boric acid as a weak electrolyte [6]. It was therefore necessary to begin by independently demonstrating this view to be incorrect. This was confirmed by the potentiometric titration curves of boric acid and nickel sulfate solutions and mixtures thereof. Experience has shown the buffer branches of potentiometric titration curves of pure boric acid and nickel sulfate solutions to appear at much higher pH than in solutions containing a mixture of nickel sulfate and boric acid.

This difference in the curves cannot be explained other than by the assumption that the composition of the solid phase is qualitatively different in the presence of boric acid than when it is absent from the solution.

If, in the general case, the composition of the solid phase be represented by the formula $x\mathrm{NiSO_4}\cdot y\mathrm{Ni(OH)_2}\cdot z\mathrm{H_3BO_3}$ and if it be considered that this compound is in equilibrium with the solution*, i.e.,

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* We are considering only the first stage dissociation of boric acid.

$$zH^+ + zH_2BO_3' + (x + y)\,Ni^{++} + 2yOH' + xSO_4'' \rightleftharpoons xNiSO_4 \cdot yNi(OH)_2 \cdot zH_3BO_3, \qquad (2)$$

the following may be written:

$$z\Delta Z_6^0 + RT\ln a_{H+}^z + z\Delta Z_7^0 + RT\ln a^z_{H_2BO_3'} + (x + y)\Delta Z_2^0 + RT\ln a_{Ni^{++}}^{(x+y)} + 2y\Delta Z_3^0 + RT\ln a_{OH'}^{2y} + x\Delta Z_4^0 + $$
$$+ RT\ln a^x_{SO_4''} = \Delta Z_5^0. \qquad (3)$$

In Equation (3) the activity of the solid phase is as usual taken as unity. ΔZ_2^0, ΔZ_3^0, ΔZ_4^0, ΔZ_6^0, ΔZ_7^0 and ΔZ_5^0 represent the standard isobaric potentials at which Ni^{++}, OH', SO_4'', H^+, H_2BO_3' and the slightly soluble compounds are formed.

As

$$K_{H_3BO_3} = \frac{a_{H^+}\,a_{H_2BO_3'}}{a_{H_3BO_3}} \qquad (4)$$

and

$$a_{OH'} = \frac{K_W}{a_{H^+}}, \qquad (5)$$

therefore

$$z\Delta Z_6^0 + z\Delta Z_7^0 + RT\ln K^z_{H_3BO_3} + RT\ln a^z_{H_3BO_3} + (x+y)\Delta Z_2^0 + RT\ln a^{x+y}_{Ni^{++}} + 2y\Delta Z_3^0 + RT\ln K_W^{2y} - RT\ln a_{H^+}^{2y} + x\Delta Z_4^0 +$$
$$+ RT\ln a^x_{SO_4''} = \Delta Z_5^0 \qquad (6)$$

or

$$pH = \frac{\Delta Z_5^0 - (x+y)\Delta Z_2^0 - 2y\Delta Z_3^0 - x\Delta Z_4^0 - z\Delta Z_6^0 - z\Delta Z_7^0}{2.3 \cdot 2yRT} - \frac{z}{2y}\lg a_{H_3BO_3} - \frac{1}{2y}\log\ a_{Ni^{++}}^{(x+y)} a^w_{SO_4''} - \lg K_W - \frac{z}{2y}\lg K_{H_3BO_3}. \qquad (7)$$

As

$$\Delta Z_5^0 - (x+y)\Delta Z_2^0 - 2y\Delta Z_3^0 - x\Delta Z_4^0 - z\Delta Z_6^0 - z\Delta Z_7^0 = \Delta Z^0_{st} \qquad (8)$$

Z^0 is the standard isobaric potential of reaction (2), $a = m\gamma$, $m_{SO_4''} = m_{Ni^{++}} = m_c$ (m=the molality of the salts and ions; γ = the coefficient of activity), equation (7) may be rewritten as follows:

$$pH = \frac{\Delta Z^0_{st}}{2.3 \cdot 2yRT} - \frac{z}{2y}\lg a_{H_3BO_3} - \frac{2x + y}{2y}\lg a_+ - \lg K_W - \frac{z}{2y}\lg K_{H_3BO_3}. \qquad (9)$$

Equation (9) was derived for a particular case; however, it may be worked out without difficulty in a general form applicable to complex slightly soluble compounds, regardless of composition. It differs from formula (1) not only in the presence of supplementary constants, but in the presence of the pH ratio to concentration of the second component of the solution – boric acid.

We conducted experiments of this type at 10 and 50°. Determination of pH, in equilibrium with the solid phase, was by potentiometric titration [3], subsequent to prior determination that slightly soluble compounds in equilibrium are not formed in this situation. This was confirmed by the fact that the pH values for the moment of formation of the solid phase and the equivalent pH values we obtained by the Gromov method, coincided.

Tables 1 and 2 show the results of our experiments. Boric acid activity is always equated to concentration. The data in Tables 1 and 2 were used to plot the pH–$\lg a_+$ and pH–$\lg C_{H_3BO_3}$ (Figs. 1 and 2).

These figures show that $\frac{2x + y}{2y} = 0.5$ and $\frac{z}{2y} = 1$.

The former equation gives x = 0 and a minimum integer value, y = 1.

Combination of the two equations gives z = 2. Consequently, the composition of the solid phase is $Ni(OH)_2 \cdot 2H_3BO_3$. It is interesting to note that this formula corresponds to that of the slightly soluble nickel diborate $NiB_2O_4 \cdot xH_2O$ [5].

TABLE 1

Ratio of pH at Moment of Solid Phase Formation to Activity of Nickel Sulfate in Solution (Concentration H_3BO_3 20 g/l)

Nickel concentration				pH	
(g/l)	(M)	$\gamma_{\pm}$	$a_{\pm}$	20°	50°
0.5	0.008	0.425	0.00361	5.22	4.75
1.0	0.017	0.340	0.00578	5.18	4.64
5.0	0.085	0.180	0.01534	4.94	4.44
10	0.170	0.120	0.02045	4.92	4.35
20	0.341	0.075	0.02556	4.88	4.24
30	0.515	0.065	0.03345	4.82	4.26
40	0.681	0.055	0.03748	4.76	4.22
50	0.852	0.050	0.04259	4.64	4.12
60	1.022	0.045	0.04600	4.60	4.04

TABLE 2

Ratio of pH at Moment of Solid Phase Formation to Concentration of Boric Acid in Solution (Concentration Ni 30 g/l)

H_3BO_3 concentration		pH	
(g/l)	(M)	20°	50°
2	0.032	5.66	5.06
4	0.064	5.48	4.82
8	0.128	5.18	4.54
12	0.192	4.96	4.36
20	0.323	–	4.20
25	0.404	4.50	4.06
35	0.566	4.44	3.88
45	0.727	4.26	3.73
55	0.889	–	3.60

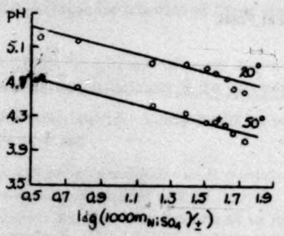

Fig. 1. Ratio of pH to logarithm of nickel sulfate activity (at 20 and 50° and at a constant concentration of boric acid, 20 g/l). The cross represents data from source [3].

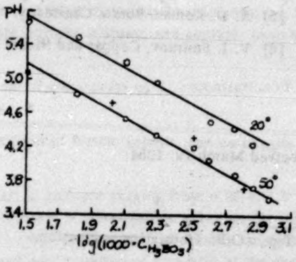

Fig. 2. Ratio of pH to logarithm of boric acid concentration (at 20 and 50° and a constant nickel sulfate concentration, 0.514 M.).

As the solid phase formed is in equilibrium with the solution, the standard isobaric potential of nickel diborate anhydride formation may be computed.

The first series of measurements at 20° provided a value of −55.0 Cal/mole, and the second −54.0 Cal/mole. As the standard isobaric potential of nickel hydroxide formation is −18.9 Cal/mole [1], the standard isobaric potential of association(ΔZ_n^0) of two boric acid moles to one of nickel hydroxide would be −36.1 Cal.

This magnitude is greater than ΔZ_n^0 when nickel sulfate associates with nickel hydrate to form $3NiSO_4 \cdot 4Ni(OH)_2$ (−20.4 Cal [2]), so that when boric acid is present and there is a gradual precipitation of nickel hydroxide, it is nickel diborate that forms to begin with, and not the basic salt.

As may readily be seen from Figs. 1 and 2, the angle coefficients of the straightlines pH-log $\underline{a}$ do not change with change from 20 to 50°.

This makes it possible to contend that the composition of a slightly soluble compound does not vary with rising temperature. The pH temperature coefficient at the beginning of formation of the solid phase in these experiments is 0.2 pH unit per 10°, which is somewhat lower than previous measurement of this magnitude (0.26 pH unit per 10° [3]).

SUMMARY

1. Potentiometric titration was used to study the composition of the solid phase at the moment of the beginning of its formation, when nickel was precipitated by a base from mixed solutions of nickel sulfate and boric acid.

2. It has been shown that in the entire concentration interval studied, the solid phase, in equilibrium with the solution, consists of nickel diborate $Ni(OH)_2 \cdot 2H_3BO_3$. Basic nickel salts in pseudo equilibrium do not form in the presence of boric acid.

3. Computations of the standard isobaric potentials of nickel diborate formation from ions and from nickel hydroxide and boric acid have been made, and it was demonstrated that the first compound to be formed must be nickel diborate, and not the basic nickel salt.

4. Elevation of temperature to 50° did not change the composition of the solid phase precipitated.

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THE PROBLEM OF ANODE DEPOSITS RESULTING FROM SILVER SALT ELECTROLYSIS. I.

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Up to the present time the problem of composition and structure of anodic silver deposits resulting from electrolysis of aqueous solutions of its salts on a platinum anode has not been given a final solution.

In the meantime, the anodic deposit is most interesting from a theoretical viewpoint and may have practical utility as a good oxidant, and as starting material for preparation of silver dioxide, and a series of molecular and complex compounds of di- and tri-valent silver.

Deposition of silver compounds upon the anode, along with deposition on the cathode, can also play a role in silver refining, as a substitute for cyanide baths; using the same amount of energy, the silver yield during electrolysis, for example of silver nitrate, with subsequent processing of the anodic deposit, is increased 1.6 - 1.7 fold.

In the present work, the composition, sturcture and conditions for formation of anodic deposits resulting from electrolysis of aqueous solutions of silver nitrate, fluoride, perchlorate, sulfate, chlorate and acetate have been studied.

Conditions for synthesis of anode deposits depend upon the amount of electrolyte used, concentration of the latter, on the form and dimensions of the electrolyzer and the electrodes.

In all case, current density should be such as to ensure only the form of anodic deposit, and no oxygen evolution should be observed.

The authors electrolyzed 1-2 N solutions of the corresponding salt in amounts ranging from 0.25 to 1.0 liter, at a current density from 0.05 to 0.20 A/cm². The exception was in the case of silver sulfate solution, for which special conditions are necessary because of its low solubility. In order to avoid dissolution of the anode deposits, electrolysis should be carried out with cooling of the electrolyzer (3-5°), and accumulation of free acid at the anode should not be permitted, as it will cause the deposit to dissolve. To avoid concentration polarization, the electrolyte should be stirred.

During electrolysis of the above-indicated salts, apart from silver acetate, there also formed on the anode well-defined, black crystals, which were quite stable at ordinary temperature, and particularly so in the dark.

From the photographs given (enlarged 200 x), it can be seen that the deposits from nitrate solutions (Fig. 1) and silver fluoride (Fig. 2) crystallize in the form of octahedrons, and from perchlorate (Fig. 3) apparently as cubes. Debye crystallograms were taken of all deposits; a Debye crystallogram of the silver nitrate deposit was confirmed by the data of Zhdanov and Zvcnkova [1] for the nitrate deposit lattice. The lattices for solutions of the fluoride and perchlorate deposits were identical with the nitrate lattice. Crystals of these deposits belong to the cubical system and posses a cubic, face-centered lattice with the constants $a_{AgNO_3} = 9.87$ Å, $a_{AgF} = 9.80$ Å, $a_{AgClO_4} = 9.90$ Å.

There are practically no data in the literature [2] on the composition of anodic deposits resulting from silver fluoride, perchlorate, sulfate, chlorate and acetate solutions; there are a sufficient number of works on the study of silver nitrate deposit composition. The composition $2Ag_3O_4 \cdot AgNO_3$ [1,3,4] attributed to this deposit, based upon a large number of analyses, can at the present time be considered as established.

However, there is no uniform answer in the literature with regards to the valency of silver in this compound. Thus, Boky and Smirnova [5] consider, on the basis of crystallochemical analysis, that two types of silver ions are present in this compound: monovalent and divalent. They attribute the formula $4AgO \cdot 2AgO_2 \cdot AgNO_3$ to this deposit, with the presence of two peroxide ions $2(O_2'')$.

The author's data for complete analyses of the anode deposit obtained from silver nitrate are given in Table 1.

The data obtained on percentage composition of the substance composing the deposit, given in Table 1, are confirmed by the following proposed reactions.

Roasting

$$2Ag_3O_4 \cdot AgNO_3 \rightarrow \underset{\substack{\uparrow\\(79.90\%)}}{7Ag} + NO_2 + \underset{\substack{\uparrow\\(15.24\%)}}{9O}. \tag{1}$$

Heating to 165-170°

$$2Ag_3O_4 \cdot AgNO_3 \rightarrow 3Ag_2O \cdot AgNO_3 + \underset{\substack{\uparrow\\(8.47\%)}}{5O}. \tag{2}$$

Roasting of the residue after heating at 165-170°

$$3Ag_2O \cdot AgNO_3 \rightarrow \underset{\substack{\uparrow\\(87.28\%)}}{7Ag} + NO_2 + 4O. \tag{3}$$

Heating with hot water

$$2Ag_3O_4 \cdot AgNO_3 \rightarrow \underset{\substack{\uparrow\\(68.49\%)}}{3Ag_2O_2} + \underset{\substack{\uparrow\\(11.42\%)}}{AgNO_3} + \underset{\substack{\uparrow\\(3.39\%)}}{2O}. \tag{4}$$

TABLE 1

Element being determined	Found (in %)	Calculated (in %)
Total amount of silver	79.90	79.90
Amount of oxygen evolved at 165-170°	8.68	8.47
Amount of oxygen evolved on boiling with water	3.15	3.39
Amount of Ag^+ washed out with hot water	11.39	11.42
Amount of silver in the residue after treatment with hot water	68.67	68.49
Amount of nitrogen	1.41	1.48
Total silver in the residue after removal of oxygen from the higher silver oxides	87.48	87.28
Amount of oxygen evolved on roasting	15.38	15.24
Total amount of oxygen	18.72	18.62
Amount of oxygen involved in oxidation of the oxalic acid	6.75	6.77
Ag_a/Ag_c	0.70	0.70

It can be seen from reactions (2) and (4) that for the compound being investigated, the oxygen present is bound with silver in various ways. The author considers that at 100° (boiling with water, Reaction 4), the oxygen which is bound to trivalent silver is reduced to divalent (known as silver dioxide, Ag_2O_2 [6], stable at 100°). At 165-170°, the oxygen which is bound to di and tri-valent silver is evolved, and the oxide of monovalent silver (Reaction 2) is formed.

The reaction with oxalic acid proved to be of interest. Of the 5 active oxygen atoms in the deposit (8.47%), only 4 (6.77%) participated in the oxalic acid oxidation. If the formula proposed by Boky and Smirnova is adopted, and if it be considered that the oxygen from silver peroxide (AgO_2) participated in the oxidation of oxalic acid, and since silver dioxide does not give constant results in oxalic acid oxidation [7], then the oxidation should go to 2 oxygen atoms if reduction of $2AgO_2$ proceeds to $2AgO$, or 3 oxygen atoms if the reduction proceeds to Ag_2O.

Experiment showed, as indicated above, that 4 oxygen atoms are used for oxidation of the oxalic acid. The authors assume that the composition of the anodic deposit can be represented as a double salt of silver nitrate with the silver salt of the silver acid corresponding to trivalent silver, similar to that for the gold acid, $HAuO_2$, namely $2Ag^{II}(Ag^{III}O_2)_2 \cdot AgNO_3$. In such case, only trivalent silver should participate in the oxidation of oxalic acid, and reaction should proceed according to the acheme:

$$\begin{array}{l}
2Ag(AgO_2)_2 + 2H_2C_2O_4 \rightarrow 2AgC_2O_4 + \underset{\substack{\downarrow\\(2H_2O + 2Ag_2O_3)}}{4HAgO_2} \\
2Ag_2O_3 + 2H_2C_2O_4 \rightarrow 2Ag_2C_2O_4 + 4O + 2H_2O \\
\underline{4H_2C_2O_4 + 4O \rightarrow 8CO_2 + 4H_2O}, \\
2Ag(AgO_2)_2 + 8H_2C_2O_4 \rightarrow 2AgC_2O_4 + 2Ag_2C_2O_4 + 8CO_2 + 8H_2O
\end{array}$$

Fig. 1. Deposit from $AgNO_3$ solution.

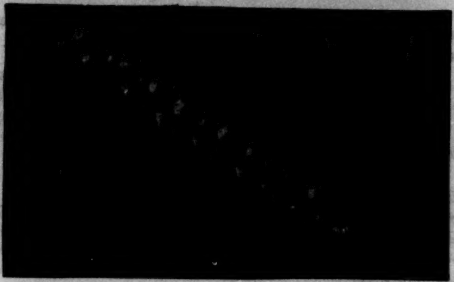

Fig. 2. Deposit from AgF solution.

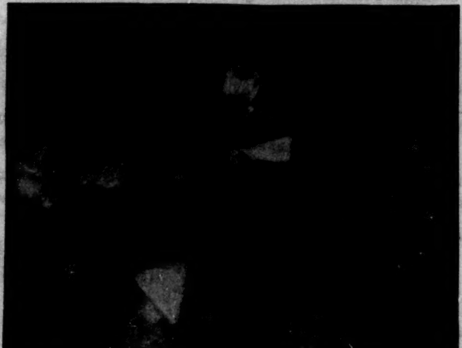

Fig. 3. Deposit from $AgClO_4$ solution.

with formation of mono- or of divalent silver oxalate. The existence of AgC_2O_4 is quite possible, by analogy with $Ag(CH_3COO)_2$ [8].

From a determination of the composition and the proposed structure for silver compounds being deposited upon the anode, the authors have proposed a method for determination of the ratio between the amount of silver which goes into the composition of the anode deposit (Ag_a) and the amount of silver being deposited within the same time on the cathode (Ag_c). This ratio should be determined only in those cases where a deposit is formed only on the anode, and no oxygen evolution is observed.

If the composition $2Ag(AgO_2)_2 \cdot AgNO_3$ is attributed to the deposit on the anode, then the monovalent silver should go into the anode as divalent and trivalent; furthermore, if the anode deposit does indeed correspond to the above given formula, and 2 divalent silver atoms and 4 trivalent silver atoms are found in it, then the total loss of electrons by silver upon its oxidation on the anode is equal to 10.

$$2Ag^{+} \xrightarrow{-2e} 2Ag^{++}$$

$$\underline{4Ag^{+} \xrightarrow{-8e} 4Ag^{+++}}$$

$$\text{Total } -10\ e$$

Since the anode has accepted 10 electrons, the cathode therefore should give up the same number of electrons, i.e., 10 atoms of silver should be deposited on the cathode.

$$10Ag^{+} + 10e \rightarrow 10Ag^{0}.$$

Hence the ratio of anodic silver to cathodic silver, Ag_a / Ag_c should be equal to 0.70. With a large number of experiments, the authors were able to confirm this ratio for silver nitrate.

The authors used a similar method of calculation for determination of the composition of anodic deposit resulting from silver fluoride. The ratio of Ag_a / Ag_c was found equal to 0.70; it follows thus that the formula $4Ag_3O_4 \cdot 3AgF$ proposed by Tanatar [9] is not accurate because with such a formula this ratio should be equal to 0.75 and the total content of silver should constitute 83.79% and not 79.60%, as the experiment indicated.

TABLE 2

Element determined	Found (in %)	Calculated (in %)
Total amount of silver	79.60	79.56
Fluoride	3.97	4.00
Total amount of oxygen	13.28	13.48
Amount of oxygen evolved on heating to 135-140°	8.41	8.43
Amount of silver in the deposit after heating deposit at 135-140°	86.72	86.98
Amount of water of crystallization	2.68	2.85
Amount of oxygen participating in oxidation of the oxalic acid	6.73	6.74
Ag_a / Ag_c	0.70	0.70

Data on determination of the individual elements in this compound (Table 2), which were not given by Tanatar, made it possible for the authors to attribute the formula $2Ag(AgO_2)_2 \cdot AgF \cdot HF \cdot 1\frac{1}{2}H_2O$ to this compound.

By investigating the crystals obtained from silver perchlorate via the same methods as were used with the nitrate and fluoride, the authors came to the conclusion (Table 3) that they should have the formula $2Ag_3O_4 \cdot AgClO_4$.

Heating at 125-130°.

$$2Ag_3O_4 \cdot AgClO_4 \rightarrow 3Ag_2O \cdot AgClO_4 + \underset{(8.14\%)}{\underset{\uparrow}{5O}}.$$

Heating with hot water

$$2Ag_3O_4 \cdot AgClO_4 \rightarrow \underset{(65.87\%)}{\underset{\uparrow}{3Ag_2O_2}} + \underset{(10.98\%)}{\underset{\uparrow}{AgClO_4}} + \underset{(3.26\%)}{\underset{\uparrow}{2\,O}}.$$

TABLE 3

Element determined	Found (in %)	Calculated (in %)
Total amount of silver	76.80	76.85
Amount of oxygen evolved at 125-130°	8.22	8.14
Amount of silver (Ag^+) washed out with hot water	10.99	10.98
Amount of silver in residue after treatment with hot water	65.56	65.87
Amount of oxygen evolved upon boiling with water	3.10	3.26
Ag_a / Ag_c	0.70	0.70

The oxidation reaction of oxalic acid indicates for oxidation of the latter, that 4 oxygen atoms are not used, as might have been expected by analogy with nitrate and fluoride deposits, but instead, 3 oxygen atoms. Evidently the anodic deposit from perchlorate possesses a somewhat different structure, as evidenced by its different crystalline form as well.

SUMMARY

1. Upon electrolyzing aqueous solutions of silver nitrate, fluoride and perchlorate on a platinum anode, crystalline black deposits, with metallic lustre are formed, stable at normal temperature.

2. The use of a method for determining the ratio of silver entering into composition of the anodic deposit to the amount of silver being deposited within the same period at the cathode has been propoæd the authors, and a detailed chemical investigation of the deposits has allowed them to make a proposal of the following formula for these substances:

1. $2Ag(AgO_2)_2 \cdot AgNO_3$,
2. $2Ag(AgO_2)_2 \cdot AgF \cdot HF \cdot 1\frac{1}{2}H_2O$,
3. $2Ag_3O_4 \cdot AgClO_4$.

3. Crystals of the resulting deposit belong to the cubical system, possess a cubic face-centered cell, with the constants for nitrate deposit of 9.87 Å, for fluoride of 9.80 Å, and for perchlorate 9.90 Å.

4. The composition of the anodic deposits does not depend upon the current density, the electrolyte concentration, or the temperature, under those conditions of electrolysis where there is formed only the deposit at the anode, and no other reactions occur.

5. The ratio of Ag_a / Ag_c under those anodic conditions where only a deposit is formed is equal to 0.7 for the deposits.

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NIOBATES AND TANTALATES OF THE ALKALI EARTH METALS. II.

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The literature describes a relatively small number of aqueous salts of the niobium and tantalum acids; they include the hexaniobates of lithium [1,3], sodium and potassium [2], and also the hexatantalates of sodium and potassium [4]. In addition to the foregoing salts, there are references to barium hexaniobate $Ba_7Nb_{12}O_{37} \cdot 18H_2O$[2], and barium hexatantalate $Ba_4Ta_6O_{19} \cdot 6H_2O$ [6], having been found.

We have obtained the hexaniobates and hexatantalates of all the alkali earth metals, although the majority of them had never been described previously in the literature.

EXPERIMENTAL

1. Initial Materials

Niobium pentoxide and tantalum pentoxide. To obtain the hexaniobates and hexatantalates of the alkali earth metals we made use of pure niobium and tantalum pentoxides, separated out and purified by the methods we described in a series of communications [5,6,7].

Sodium hexaniobate, $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$. 8 g calcined niobium pentoxide were fused in a silver cup with 32 g caustic soda. After cooling, the resultant melt was pulverized and washed with water to remove the excess caustic soda. The salt residue $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$ was dissolved in water while heated, filtered and concentrated to a small volume. After the addition of an equal volume of alcohol, a residue of sodium hexaniobate was precipitated out. The salt was filtered and washed with alcohol and ether. Analysis showed the salt thus obtained to have the composition: $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$.

Potassium hexatantalate $K_{16}Ta_{12}O_{38} \cdot 33H_2O$. 10 g tantalum pentoxide were fused with 30 g pulverized caustic potash, water then being used to remove the excess alkali from the melt. The salt residue was filtered, washed with alcohol and dissolved in water, the solution then filtered and concentrated to half its volume. The addition of an equal volume of alcohol resulted in the precipitation of potassium hexatantalate. The composition of the salt was confirmed by analysis.

2. Preparation of the Hexaniobates and Hexatantalates of the Alkali Earth Metals

Hexaniobates of the alkali earth metals. These salts were obtained by adding nitrates of calcium, strontium and barium (chem. pure) to sodium hexaniobate solution. It was noted that the rate of formation of precipitates varied. The barium salt was the most rapidly precipitated, and the calcium – the most slowly. The salts obtained were analyzed for metallic oxide, niobium pentoxide, and water content. The metallic oxide was determined as the sulfate, while the niobium pentoxide – as usual [5]. The water content was arrived at by the determination of constant weight upon the calcination of the salt samples. The results of chemical analysis of the hexaniobates of the alkali earth metals follow.

Analysis of calcium hexaniobate.

Sample of substance 0.2734 and 0.2056 g.

Found %: CaO 15.08, 15.14; Nb_2O_5 63.74, 63.88; H_2O 21.00, 20.94. $Ca_7Nb_{12}O_{37} \cdot 30\ H_2O$. Calculated %: CaO 15.29; Nb_2O_5 63.68; H_2O 21.03.

Analysis of strontium hexaniobate.

Sample of substance 0.2830 and 0.2247 g.

Found %: SrO 25.68, 25.34; Nb_2O_5 56.24, 56.62; H_2O 18.04, 18.30. $Sr_7Nb_{12}O_{37} \cdot 29\ H_2O$. Calculated %: SrO 25.50; Nb_2O_5 56.08; H_2O 18.42.

Analysis of barium hexaniobate.

Sample of substance 0.2166 and 0.2454 g.

Found %: BaO 33.70, 33.38; Nb_2O_5 49.52, 49.80; H_2O 16.60, 16.94. $Ba_7Nb_{12}O_{37} \cdot 30H_2O$. Calculated %: BaO 33.46; Nb_2O_5 49.71; H_2O 16.83.

The analytical results show that exchange reactions between nitrates of the alkali earth metals and sodium hexaniobate result in salts of the following composition:

$$Ca_7Nb_{12}O_{37} \cdot 30H_2O,\ Sr_7Nb_{12}O_{37} \cdot 29\ H_2O,\ Ba_7Nb_{12}O_{37} \cdot 30H_2O.$$

Hexatantalates of the alkali earth metals. These salts were obtained in the same manner as in the previous case. The hexatantalates of calcium, strontium and barium formed by the reaction of the corresponding nitrate with sodium hexatantalate, were gelatinous white precipitates. The precipitates were filtered, carefully washed with water and air-dried to a constant weight.

Results of analysis of the salts follow.

Analysis of calcium hexatantalate

Sample of substance 0.1862 and 0.3208 g.

Found %: CaO 12.30, 12.23; Ta_2O_5 71.16, 71.88; H_2O 16.11, 16.04. $Ca_8Ta_{12}O_{38} \cdot 33H_2O$. Calculated %: CaO 12.12; Ta_2O_5 71.91; H_2O 15.97.

Analysis of strontium hexatantalate

Sample of substance 0.2502 and 0.2480 g.

Found %: SrO 20.53, 21.12; Ta_2O_5 65.52, 64.59; H_2O 14.44, 14.11. $Sr_8Ta_{12}O_{38} \cdot 33\ H_2O$. Calculated %: SrO 20.40; Ta_2O_5 65.03; H_2O 14.57.

Analysis of barium hexatantalate

Sample of substance 0.2238 and 0.3116 g.

Found %: BaO 27.34, 27.08; Ta_2O_5, 59.60, 59.29; H_2O 13.06, 13.42. $Ba_8Ta_{12}O_{38} \cdot 33H_2O$. Calculated %: BaO 27.38; Ta_2O_5 59.33; H_2O 13.29.

The data show that we obtained the hexatantalates of calcium: ($Ca_8Ta_{12}O_{38} \cdot 33H_2O$), strontium ($Sr_8Ta_{12}O_{38} \cdot \cdot 33H_2O$) and barium ($Ba_8Ta_{12}O_{38} \cdot 33\ H_2O$).

Conductometric titration. Conductometric titration was undertaken for quantitative verification of exchange reaction results in preparing the hexaniobates and hexatantalates of the alkali earth metals. Some changes were made in the usual design of the apparatus for determining the electrical conductivity of a solution: the Wheatstone bridge was replaced by two resistance boxes, and an oscillograph took the place of the headphones used to determine the sound minimum. The end of the exchange reaction was determined when minimum amplitude of oscillation was reached.

Titration curve minimums noted in all cases confirmed simple replacement of base metal by alkali earth in hexaniobate and hexatantalate without change in oxide relationships in salt molecules, representing a verification of the chemical analysis results.

Determination of alkali earth metal hexaniobate and hexatantalate saturated solution electrical conductivity. As the salts obtained were of weak solubility, we decided to determine the specific conductivity of saturated solutions of all the compounds we had derived.

Determination of alkali earth metal metaniobate and metatantalate saturated solution electrical conductivity was performed by means of a conductometric titration apparatus at 20°.

A bi-distillate* was used to prepare saturated solutions of the salts under investigation. Each value for specific conductivity adduced in the table represents an average of 3 or 4 measurements.

The absence of data on the mobility of the $Nb_{12}O_{37}^{-14}$ and $Ta_{12}O_{38}^{-16}$ ions in the literature made it impossible to compute the solubility values of these salts.

Air-dried hexaniobates of calcium, strontium and barium and hexatantalates of calcium, strontium and barium were subjected to roentgenographic study by means of powdergrams. All the radiograms showed an absence of lines, permitting the conclusion that these compounds are roentgenamorphous. After calcination at temperatures over 400°

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* The specific conductivity of the bi-distillate was $1.4 \cdot 10^{-6}$ ohm $^{-1}$ am $^{-1}$.

TABLE
Specific Electrical Conductivity of Alkali Earth Metal Metaniobate and Metatantalate Saturated Solutions at 20° (beaker constant 0.4439)

Compound	Electrical conductivity	
	Equivalent	Specific
$Ca_7Nb_{12}O_{37} \cdot 30H_2O$	$5.8 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$
$Sr_7Nb_{12}O_{37} \cdot 29H_2O$	$1.85 \cdot 10^{-5}$	$8.2 \cdot 10^{-6}$
$Ba_7Nb_{12}O_{37} \cdot 30H_2O$	$2.00 \cdot 10^{-5}$	$9.0 \cdot 10^{-6}$
$Ca_8Ta_{12}O_{38} \cdot 33H_2O$	$1.84 \cdot 10^{-5}$	$8.19 \cdot 10^{-6}$
$Sr_8Ta_{12}O_{38} \cdot 33H_2O$	$1.72 \cdot 10^{-5}$	$7.62 \cdot 10^{-6}$
$Ba_8Ta_{12}O_{38} \cdot 33H_2O$	$1.43 \cdot 10^{-5}$	$6.39 \cdot 10^{-6}$

samples of all salts under study showed clearly defined lines coinciding completely with the lines of alkali earth metals, anhydrous metaniobates and metatantalates, indicating the decomposition of these salts upon heating.

SUMMARY

1. The hexaniobates of calcium and strontium, and hexatantalates of calcium, strontium and barium were produced for the first time.

2. The specific electrical conductivity of solutions, saturated at 20°, of hexaniobates and hexatantalates of all the alkali earth metals, was determined.

3. It was shown that alkali earth metal hexaniobates and hexatantalates are thermally unstable at temperatures over 400°.

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* T.p. = C.B. Translation pagination.

T A B L E

Specific Electrical Conductivity of Alkali Earth Metal Hexaniobates and Hexatantalates Saturated Solutions at 25°

[illegible]

Compound	Electrical conductivity	
	[illegible]	Specific
$Ca_4Nb_6O_{19}\cdot 20H_2O$	[illegible]	[illegible]
$Sr_4Nb_6O_{19}\cdot 22H_2O$	[illegible]	[illegible]
$Ba_4Nb_6O_{19}\cdot 20H_2O$	[illegible]	[illegible]
$Ca_4Ta_6O_{19}\cdot 22H_2O$	[illegible]	[illegible]
$Sr_4Ta_6O_{19}\cdot 25H_2O$	[illegible]	[illegible]
$Ba_4Ta_6O_{19}\cdot 20H_2O$	[illegible]	[illegible]

samples of all salts under study showed a [illegible] defined [illegible] alkali earth metals anhydrous metaniobates and metatantalates [illegible]

[illegible]

1. The hexaniobates of calcium and strontium, and hexatantalates of calcium, strontium and barium [illegible] for the first time.

2. The specific electrical conductivity of saturated solutions of [illegible] of all the alkali earth metals was determined.

3. It was shown that all alkali earth metal [illegible] temperature over 400°.

L I T E R A T U R E   C I T E D

[illegible]

FACTORS DETERMINING STABILITY OF CERTAIN TYPES OF COMPLEX COMPOUNDS IN AQUEOUS SOLUTIONS

K. B. Yatsimirksy

There has accumulated during the last few years quite a significant amount of material on the stability of complex compounds in aqueous solutions. Instability constants have been determined for 700-800 complex ions. The existence of such a tremendous mass of factual material makes it possible to pose the question of elucidation of factors determining stability of the groups of complex compounds which have received the most study. Those complex compounds are considered whose central atoms can form stable hydrated ions (complex compounds of silver, copper, aluminum and other metals). Complex compounds of platinum, gold antimony, tetravalent lead, and some of the platinum group metals, on dissociation in aqueous solutions, do not form hydrated ions and are not considered in this paper.

For complex compounds forming hydrated ions upon dissociation, the chemical bond approximates the ionic type, the central atom preserving the properties of the ions to a considerable extent, and in such cases central atoms can be mentioned as well as central ions.

The stability of complex compounds with some additives, for the cases investigated, is determined by such characteristics of the central ions as charge, radius, and its polarizability (ability to deform the electronic shell of the additive atoms, with tendency to covalent bond formation). To clarify the role of various factors, it was expedient to investigate a group of complex ions with the same additives in which only one characteristic of the central ions is changing (charge, radius or polarizing action), and two others of approximately the same stability.*

In order to elucidate the effect of charge upon the stability of complex compounds, three sets of cations of approximately the same dimensions were chosen: 1) Na^+, Ca^{2+}, Y^{3+}, Th^{4+} (cation radius $r_c = 1.04 \pm 0.06$ A), 2) K^+, Sr^{2+}, La^{3+} ($r_c = 1.27 \pm 0.06$ A) and 3) Ag^+, Hg^{2+}, Tl^{3+} ($r_c = 1.09 \pm 0.04$ A).

In the first two sets, the cations possess a complete shell of eight electrons and low oxidizing potential, and in the third set the cations possess a shell of eighteen electrons, with approximately the same oxidizing potential (about 0.8 v.). It can be assumed that in a related series the polarizing action of the cations is approximately the same.

In Table 1 are given values for the indices of instability constants ($pK = -\log K_{instab.}$) for the three series of ions. In almost all cases, pK increases with increase in charge. Particularly noticeable is the increase in pK with low or highly charged additives. The stability of complexes with large amounts of additives of low charge changes but little with a change in charge of the central ion (complex iodides, bromides, nitrates, and others).

The change in pK with change in charge proceeds so regularly that in some cases interpolation is possible. Thus, for example, values for the instability constant indices of nitrate and iodate complexes of yttrium can be evaluated: For YNO_3^{2+} $pK = 0.45 \pm 0.07$, for YIO_3^{2+} $pK = 1.9 \pm 0.3$.

To clarify the effects of other factors upon the stability of complex compounds, we might examine a little more closely the function which the author, together with Grinberg, developed [4]. It was demonstrated that the thermal effect of MA_n complex formation in aqueous solutions of a central ion, M, and additive, A, can be represented by the following equation:

$$\Delta H = W_{aq} - W_c + \text{const}_1, \qquad (1)$$

where W_{aq} and W_c = respectively, the energy of addition of nH_2O molecules and n particles of A to the central ion. It was indicated earlier [5] that the energy of addition can be presented as a sum of two factors: the energy of electrostatic attraction (W^i) and the polarization energy (P). Equation (1) can therefore be modified in the following manner:

$$\Delta H = W^i_{aq} - W^i_c + P_{aq} - P_c, + \text{const}_1. \qquad (2)$$

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* Values for instability constants are taken from the author's review article [1] and other reviews [2,3].

TABLE 1
Indices of Instability Constants for a Series of Ions with Alternating Charge

Types of complex ions	pK for the charge of the central ions (Z)			
	+1	+2	+3	+4
	K^+ Sr^{2+} La^{3+}			
ROH^{Z-1}	(−0.7)	1.0	3.3	-
$RS_2O_3^{Z-2}$	0.1	2.0	-	-
$RP_3O_9^{Z-3}$	1.2	3.4	5.7	-
$RFe(CN)_6^{Z-3}$	1.2	2.8	3.7	-
	Na^+, Ca^{2+}, Y^{3+}, Th^{4+}			
RIO_3^{Z-1}	-	0.9	-	2.9
RNO_3^{Z-1}	-	0.3	-	0.6
RSO_4^{Z-2}	0.7	2.3	3.5	4.1
$RC_2O_4^{Z-2}$	-	3.0	7.3	-
$REdta^{Z-4}$*	-	11.1	18.0	-
	Ag^+, Hg^{2+}, Ti^{3+}			
ROH^{Z-1}	2.3	10.3	14.8	-
RNH_3^{Z}	3.2	8.8	-	-
RCl^{Z-1}	2.7	5.3	8.1	-
RBr^{Z-1}	9	9.1	9.7	-

The polarization energy is calculated by means of an empirical equation of the type

$$P = n\beta\alpha\rho \qquad (3)$$

where α = polarizability of the additives, ρ = polarizing action of the cation, β = a coefficient, being determined by the additive dimensions and those of the central ion. Whereupon,

$$P_c - P_{aq} = n(\beta_c\alpha_A - \beta_{aq}\alpha_{H_2O})\rho. \qquad (4)$$

The value in parentheses is related to the relative polarizability of additive A, and will be symbolized as b'. The b' value depends not only upon the ratio between the polarizabilities of the additive and of the water (α_A and α_{H_2O}), but also depends upon the dimensions of the central ions and of the additives.

For acid complexes, we then have

$$\Delta H = \frac{A}{(r + r_W)^2} - \frac{B}{r + r_A} - nb'\rho + \text{const}_1, \qquad (5)$$

where r, r_A and r_W = the radii, respectively, of the central ion, the anion-additive and a water molecule, and A and B = constants, determined by the charges (or by the dipole moments) of the reacting particles and by the spatial configuration of the complex.

In the case of monotypical complexes, entropy change for the reaction in question fluctuates within a comparatively small range [6], and therefore a simple function exists between the instability constant and ΔH

$$RT \ln K_{\text{inst.}} \approx \Delta H + \text{const}_2. \qquad (6)$$

If a series of complexes is selected with an approximately constant polarization energy, then the effect of radius upon the ΔH value can be revealed, and as a consequence of which, the stability of the complexes. For this purpose, Equation (5) can be differentiated

$$\frac{\partial \Delta H}{\partial r} = \frac{B}{(r + r_A)^2} - \frac{2A}{(r + r_W)^3}. \qquad (7)$$

---

* Edta = ethylenediaminetetracetate.

It follows from Equation (7) that with an increase in cation radius, the stability of the complexes may increase (if the first member of the first part of the equation is smaller than the second), decrease, and pass through a maximum. An increase in stability of the complexes with increase in cation radius should be observed in the case of anion-additives of high radius values (r_A), and, contrariwise, for the case of small anions, the stability of complexes should decrease with an increase in cation radius.

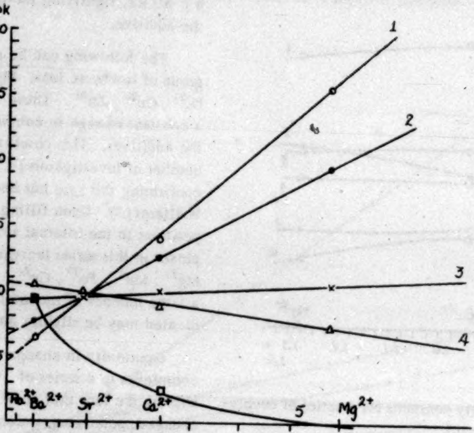

Fig. 1. Instability constant indices for a series of doubly -charged ions of varying radius. 1) MOH^+ (r_A = 1.40), 2) $MAlan^+$, 3) $MCH_3CO_2^+$ (r_A = 1.59), 4) MIO_3^+ (r_A = 1.82), 5) RNO_3^+ (r_A = 1.89).

These views are confirmed by extensive experimental material. In Figs. 1 and 2 there is shown the change in stability of complex ions formed from elements of the second main group of the Mendeleev periodic system. In the case of small singly-charged ions (r_A < 1.6 A) and α -aminoacids, the stability of the complexes changes continuously from Mg^{++} to Ba^{++}. If the radius of the anion-additive exceeds 1.6 A (nitrates, iodates) then the stability of the complex compound changes in reverse order. Apparently the same rules are observed also by doubly-charged anion-additives; stability of the oxalate complexes increases with decrease in radius, stability of succinate complexes being almost independent of the cation radius value, and finally, stability of thiosulfate complexes increasing with increase in radius. Indices for the instability constant of complexes with triply- and quadruply-charged anion-additives either do not change with change in radius, or pass through a maximum.

The mechanisms found here can be utilized to control data on stability of complex compounds, the values for certain constants being found by interpolation, and possibly by extrapolation. Such extrapolation is quite permissible according to data indicated by Shubert and other investigators[7,8].

Sulfate complexes of magnesium and calcium have approximately the same stability (pK = 2.3 ± 0.1). The sulfate ion radius = 2.30 A. Utilizing the mechanisms developed here, the author has assumed that barium and strontium also form sulfate complexes with instability constants equal to 2.3 ± 0.2 for $BaSO_4$ and $SrSO_4$. From this point of view the dissolution of $BaSO_4$ in concentrated H_2SO_4 can be explained not only by formation of an acid salt, but also by formation of a complex of the type $Ba(SO_4)_2^{2-}$.

There are no data in the literature pertaining to calcium pyrophosphate complexes, but the existance of magnesium pyrophosphate complexes has been proved [9]. Since the pyrophosphate ion charge is high, and its dimensions considerable, the existence of such complexes can be demonstrated by direct qualitative experiment: the precipitate of calcium pyrophosphate dissolved readily in excess sodium pyrophosphate.

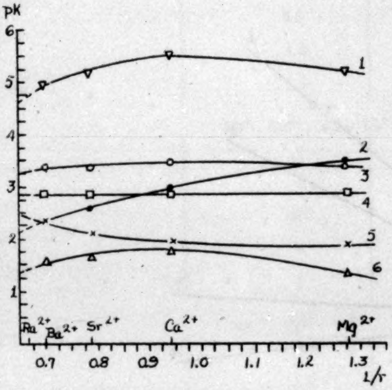

Fig. 2. Indices for instability constants for a series of doubly-charged ions with varying radii.

1) $MP_4O_{12}^{2-}$, 2) $MP_3O_9^-$, 3) MC_2O_4, 4) $MFe(CN)_6^-$, 5) MS_2O_3, 6) $MC_4H_4O_4$.

For monotypical complex compounds, formed from ions of the same charge and of approximately the same volume, the following relationship is derived from Equations (5) and (6):

$$pK = a' + nb\rho, \qquad (8)$$

where a' = a constant, including many values which do not change for a series of isochoric ions, and b = b'/RT, signifying the relative polarizability of the additive.

The following can be given as examples of the group of isochoric ions: Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}. There is preserved in this series a constant change in complex stability with any of the additives. This observation has been made by a number of investigators [4,10,11]; copius material confirming this rule has been given by Irving and Williams [3]. Upon filling one or two coordination positions in the internal sphere, stability of the complexes in this series increases in the following order: Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}. With a large number of monomial additives, the order indicated may be slightly out of line.

Continuity in change of stability for various complexes in a series of isochoric ions is explainable by the fact that only one characteristic is changed (polarizing action of the cation), the remaining being constant. For complexes with a given group of additives, there can be observed a change in stability of a determined order among ions of various radii [1,6]. However, with other additives of the series indicated, transpositions can be observed in similar fashion when an attempt is made to put into the investigated series non-isochoric ions (for example Pb^{2+} and Cd^{2+}).

Equation (8) can be utailized with that data on hand with respect to relative polarizability of additives (b), and polarizing action of the cations (ρ). A number of investigators have related the polarizing action of ions with ionization potential values [5,6,10,11]. Such dependence of course exists, but is observed only approximately, and only for isochoric ions. This dependence can be utilized only for qualitative comparisons of stability change in the series quoted.

For development of quantitative relations, the author will utilize conditional values for relative polarizability of additives, taking the polarizability of alaninate (α-aminopropionate) as equal to unity. The course of subsequent deliberations will not be altered if alaninate polarizability be taken as equal to any other constant value, or if some other additive is selected as a standard of polarizability. Choice of alaninate as the standard of polarizability was motivated by the fact that agreement in values for alaninate instability constants were independently arrived at by several investigators [12,13]. From Equation (8) one obtains

$$\rho = pK_1^0 - a', \qquad (9)$$

where pK_1^0 = index for instability of complexes of the type $MCH_3CHNH_2COO^+$ (abbreviated further to $MAlan^+$). By means of these values, as can be seen, the polarizing action for cations of the series investigated can be expressed. The pK_1^0 values are given as follows: Mg^{2+} 2.0, Mn^{2+} 3.0, Fe^{2+} 4.0,* Co^{2+} 4.8, Zn^{2+} 5.2, Ni^{2+} 6.0, Cu^{2+} 8.5.

From Equations (8) and (9) one obtains

$$pK = a + nb\, pK_1^0, \qquad (10)$$

where $a = a'(1 - nb)$.

---

* Interpolated value

Equation (10) is used for complex compounds of the type MA and MA_2 for the cases of ammoniates, alaninates, glycinates and glycylglycinates. Upon adding one particle of additive, Equation (10) is used for complexes with ethylenediamine, propylenediamine, diethylenetriamine, acetate, oxalate, malonate, succinate, hydroxyl, salicylic and sulfosalicylic aldehydes, thiosulfate, trimetaphosphate, tetrametaphosphate, iminodiacetate, iminodipropionate, iminopropionoacetate, hydroxy-ethyliminoacetate, oxyquinolate and dioxydiethylglycinate. Thus, Equation (10) has been checked on 27 series of complex compounds, certain examples being given in Figs. 3 and 4. Average deviations in pK values amount to ± 0.15.

In the cases investigated, all instability constant indices for a series of isochoric ions are related to each other by a direct linear function.

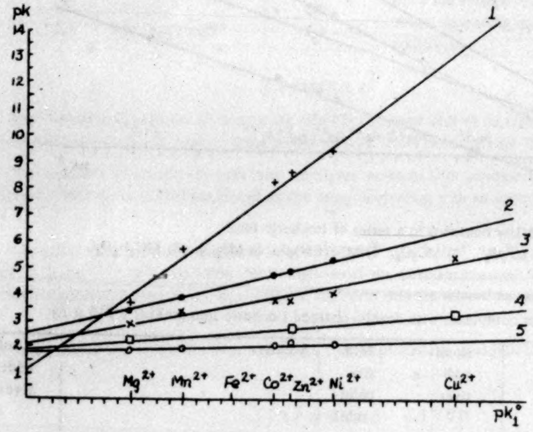

Fig. 3. Indices for instability constants in a series of isochoric ions.
1) $M[HOC_2H_4N(CH_2CO_2)_2]$, 2) MC_2O_4, 3) $MCH_2(CO_2)_2$, 4) $M(CH_2CO_2)_2$, 5) MS_2O_3.

Equation (10) is not observed, however, if more than two nitrogen or oxygen atoms enter into the internal sphere. Deviations in linear function are observed in the case of ammoniacal complexes containing more than two ammonia molecules, ethylenediamine complexes with two or more molecules of ethylenediamine, as well as with complexes of ethylenediaminotetraacetate, nitrilotriacetate and other similar additives; nevertheless, there exists in these cases a linear relationship between the indices for instability constants within a related group of complex compounds.

Constants for Equation (10) for various groups of complexes are given in Table 2; relative polarizability of additives has been calculated through a tangent of the angle of slope for the straight line, $pK - pK_1^0$.

Relative polarizability of additives is determined by the nature of the atoms, by which there is obtained a relationship between the central atoms (the lowest values for b are for additives bound to oxygen; average value – for amino acids (bound through O and N); highest b values are characteristic of additives bound to the central atom through nitrogen).

The linear functions revealed between indices for instability constants can be used as control for data at hand. For examples, we might quote data for $CoOH^+$, published in the same year and same journal. According to Gayer and Woontner [14], the pK = 1.8, and according to Chaberek Courtney and Martell [15], the pK for $CoOH^+$ is 5.1. According to Equation (10), utilizing the constants given in Table 2, the pK is 4.4.

The linear function found can also be utilized to calculate an unknown instability constant by interpolation or extrapolation. In Table 2 there are given constants of Equation 10 for 27 series of complex compounds calc., from 128 values for instability constants. Instability constant values are not known for 61 complexes, but can be evaluated to an accuracy of ± 0.3, the constants being given in Table. 2

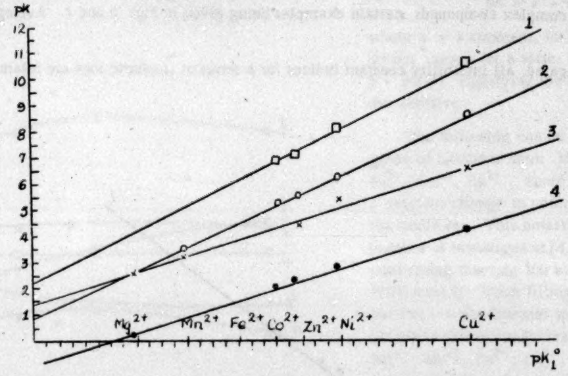

Fig. 4. Indices for instability constants in a series of isochoric ions.
1) $MP_4O_{12}^{2-}$, 2) $MP_2O_9^-$, 3) MC_2O_4, 4) $MFe(CN)_6^-$, 5) MS_2O_3, 6) $MC_4H_4O_6$.

TABLE 2

Equation (10) constant for complexes with doubly-charged isochoric ions (radius 0.8-0.9 A)

Additive	No.of additives	a	Relative polarizability	Additive	Noof additives	a	Relative polarizability
SO_4^{2-}	1	2.35	0.00	o-oxyquinolate	1	5.0	0.96
$P_3O_9^{3-}$	1	3.4	0.00	$(OHC_2H_4)_2NCH_2CO_2^-$	1	0.4	0.96
$P_4O_{12}^{4-}$	1	5.2	0.00	$H_2NCH_2CO_2^-$	1	0.9	0.90
$S_2O_3^{2-}$	1	1.8	0.06	$H_2NCH_2CO_2^-$	2	0.4	0.90
$CH_3CO_2^-$	1	0.7	0.18	$CH_3CHNH_2CO_2^-$	2	−1.0	1.00
$(CH_2CO_2)_2^{2-}$	1	1.8	0.18	$HN \left< \begin{matrix} CH_2CO_2^- \\ C_2H_4CO_2^- \end{matrix} \right.$	1	0.5	1.12
$CH_2(CO_2)_2^{2-}$	1	2.0	0.41	$HN(C_2H_4CO_2)_2^{2-}$	1	− 0.8	1.19
$C_2O_4^{2-}$	1	2.5	0.47	$HN(CH_2CO_2)_2^{2-}$	1	2.2	0.97
$C_6H_3 \left< \begin{matrix} CHO \\ SO_3^- \\ O^- \end{matrix} \right.$	1	0.0	0.62	$HOC_2H_4N(CH_2CO_2)_2^{2-}$	1	1.1	1.44
$C_6H_4 \left< \begin{matrix} CHO \\ O^- \end{matrix} \right.$	1	1.5	0.67	NH_3	1	−1.0	0.61
OH^-	1	1.4	0.62	NH_3	2	− 2.2	0.59
$NH_2CH_2COHNCH_2COO^-$ (glycyl-glycinate)	1	−0.2	0.76	$C_2H_4(NH_2)_2$	1	−1.7	1.44
$NH_2CH_2CONHCH_2COO^-$	2	− 2.0	0.80	$CH_3C_2H_3(NH_2)_2$	1	−1.7	1.44
				diethylenetriamine	1	−3.0	2.3

Some examples of such an evaluation of instability constants for ammoniacal, ethylenediamine, sulfate, thiosulfate, acetate and oxalate complexes are given in Table 3. Instability constants can be evaluated in a number of other cases by similar procedure.

The linear function for pK, as revealed by the author, can be used to predict the possibility of existence of new complexes and for evaluation of their stability. If a complex compound of given type is found in solution for magnesium, copper, and one other intermediate member of the series, and in such case the presence of a linear function between the pK's has been established, then there should also exist for the four remaining ions a complex compound of the type in question, and instability constant values for them can be determined by interpolation.

TABLE 3

Calculated instability constant values for certain complexes

Complex ion	pK	Complex ion	pK
$MnNH_3^{2+}$	0.8	$FeOH^+$	3.9
$Mn(NH_3)_2^{2+}$	1.3	$CoOH^+$	4.4
$FeNH_3^{2+}$	1.4	$MnCH_3COO^+$	1.2
$Fe(NH_3)_2^{2+}$	2.2	$FeCH_3CO_2^+$	1.4
$FeSO_4$	2.3	$NiCH_3CO_2^+$	1.8
FeS_2O_3	2.0	CuC_2O_4	6.5
FeC_2O_4	4.4	$MgC_2H_4(NH_2)_2^{2+}$	1.2

The question of the nature of additive effect upon stability of the complex compounds is found to be somewhat more complicated. The value of the additive charge (stabilization of the complex with increase in additive charge), its dimensions and polarizability play an important role, determined in first approximation by the nature of the atoms entering into the internal sphere. The entropy factor plays a considerable role in this case, since the entropy change fluctuates within a wide range, depending upon the nature and number of additives.

SUMMARY

1. The stability of complexes in aqueous solution increases with an increase in charge of the central ion. This effect is especially strong in the case of anion-additives with small radii or large charges.

2. The stability of complexes with large additives increases with increase in radius of the central ion, the stability of complexes with small additives and of amino acids decreasing with an increase in radius of the cationic complex.

3. The polarizing action of isochoric ions Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} can be characterized by means of its instability constant values for complexes of the metals enumerated with alanine (pK_1^0). Instability constant values for monotypical complexes in a series of isochoric ions are related to each other by a simple linear function.

The linear function which has been revealed can be utilized to evaluate instability constants for a series of complexes.

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COMPLEX FORMATION IN SOLUTIONS OF TERNARY SYSTEMS BY THE CRYOSCOPIC METHOD

III. $SbBr_3 - AlBr_3 - C_2H_4Br_2$ and $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$

E. Ya. Gorenbein

Cryoscopy, as a method of physico-chemical analysis, has already been used many times. Thus, for example, Plotnikov [1] studied the interaction of dimethylpyrone with trichloroacetic acid and tribromoacetic acid in benzene by the cryoscopic method. Rabinovich [2] used this method to establish solvation. Udovenko and Usanovich [3] used this method in somewhat modified form. Lately the cryoscopic method has been extensively used by Fialkov and Muzyka [4] for the purpose of studying complex formation in solution. The principle involved is based on the fact that when interaction occurs between components of a system, depression of feeezing point should not be observed, nor should it change noticeably, but when the new component added exceeds the stoichiometric ratio which corresponds to the new compounds formed, then this situation will be manifested by a bend in the freezing point lowering curve versus composition (Δt vs composition). The bend in the curve corresponds to the composition of the complex formed in the solution.

The cryoscopic method of investigation, as applied by the author, differs from thermal analysis by the fact that upon cooling there should always crystallize out in solid phase only the solvent, i.e., the component whose concentration should remain constant, and the substances entering into reaction remain in the liquid phase.

It is known from the literature that the composition of the compound being formed in solution cannot always be established by any one physico-chemical method of analysis, and that several properties therefore have to be studied in order to evaluate more accurately the presence of chemical interactions and the composition of compounds forming in the liquid phase.

Proceeding from this fact, it was of interest, naturally, to apply the cryoscopic method on the one hand to such systems as those whose components produce only one compound according to the data of other methods, and on the other hand, to such systems whose components form more than one compound. Such systems are found to be the following:

$$SbBr_3-AlBr_3-C_2H_4Br_2 \text{ and } AlBr_3-(C_2H_5)_2O-C_2H_4Br_2.$$

EXPERIMENTAL

Antimony bromide and aluminum bromide were synthesized and purified in the same manner as was described in the preceding articles [5]. The ethyl ester was prepared as previously [6]. The ethylene bromide was thoroughly purified and dried over fused calcium chloride, and distilled. All preparations were stored in sealed ampoules. The solutions were prepared in a special container with ground stopper and with side tube closed with glass rod by means of a rubber tube. For the $SbBr_3-AlBr_3-C_2H_4Br_2$ system, molten $AlBr_3$ was first introduced, followed by weighing, and then by a suspension of antimony bromide, and finally the requisite amount of solvent from a burette, controlled by weighing.

For the $AlBr_3-(C_2H_5)_2O-C_2H_4Br_2$ system, molten $AlBr_3$ was first introduced, followed by a certain amount of solvent sufficient to dissolve the $AlBr_3$, and then about the desirable amount of ether. After weighing, calculation was made to determine what amount of solvent should be added in order to obtain the desired molecular ratio of components for the system; this amount was added from a weighing burette. Dissolution of the ether in an ethyl bromide solution of aluminum bromide was accompanied by considerable thermal effect. Measurements were carried out in a Beckman apparatus, adapted for work with hydrolyzable substances. The stirrer was nickel [7]; it was set into motion by means of an electromagnet. For the system

$$AlBr_3-SbBr_3-C_2H_4Br_2$$

stirring was carried out with a glass rod. For the system

$$AlBr_3-SbBr_3-C_2H_4Br_2$$

measurements were carried out at isomolar concentration, equal to 0.1, and for the $AlBr_3-(C_2H_5)_2O-C_2H_4Br_2$ system equal to 0.05 per mole of solvent ($C_2H_4Br_2$).

The $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system

The $AlBr_3-SbBr_3$ system was investigated by melting [8], viscosity and conductivity [9] in the molten state. These investigations indicated that the compound $SbBr_3 \cdot AlBr_3$ is the electrolyte. It was of interest, naturally, to verify by the principle of isomolarity in an indifferent solvent, whether or not this compound is preserved in solution.

Aluminum bromide in ethylene bromide is associated and its degree of association does not change significantly with small change in concentration [10].

The author has investigated the change in molecular state of $SbBr_3$ in ethylene bromide upon dilution. The results are given in Table 1.

TABLE 1

The $SbBr_3-AlBr_3-C_2H_4Br_2$ system

$SbBr_3$ in all experiments was 6.6237 g.

M_{SbBr_3} / $M_{C_2H_4Br_2}$	$C_2H_4Br_2$ (in g)	Freezing point lowering (Δt)	M_{SbBr_3}
0.0993	34.67	5.53	431.6
0.0893	38.55	5.09	421.1
0.0732	47.00	4.30	409.8
0.0618	55.69	3.69	403.0

As can be seen from the data of Table 1, antimony bromide in ethylene bromide solution is somewhat associated, and the degree of association changes but little with dilution. If one compares the degree of association of both components, separately, in ethylene bromide as solvent, then the $AlBr_3$ is more associated, all other factors being equal [10]. Change in degree of association of the components upon dilution need not be considerable in order to employ cryoscopic investigation of the system.

Curve 1 of Fig. 1 reflects the relationship of freezing temperature lowering to mole percent of $AlBr_3$ and $SbBr_3$ composition, the sum of which moles was taken as 100%. The greatest freezing point lowering of the solutions corresponded to the binary sytem

$$SbBr_3-C_2H_4Br_2 \quad \text{or} \quad AlBr_3-C_2H_4Br_2.$$

As this, or other components, are added under conditions of isomolar concentration, the lowering of freezing point decreases and the lowest value, Δt, corresponds to a composition of the compound formed in solution, $SbBr_3 \cdot AlBr_3$.

In addition, other properties (viscosity, electroconductivity) which were studied by the author, together with Smolentsev [11], for the same system, except at another isomolar concentration equal to 0.4 per mole of ethylene bromide, are compared.

It can be seen on the curves of Fig. 1 that the maxima for corrected κ' (Curve 4) and specific electroconductivity, κ (Curve 2) uncorrected for viscosity, as well as viscosity, η, (Curve 3), and the maximum depression, Δt, (Curve 1), correspond to an equimolecular composition for the compound forming in solution.

The results obtained indicate without doubt that the electrolyte in this solution, independent of isomolar concentration of 0.1 or 0.4, is found to be the $SbBr_3 \cdot AlBr_3$ complex.

The molecular weight of this complex, proceeding from the depression, corresponding to an equimolecular composition of components $AlBr_3$ and $SbBr_3$, is equal to 453.5, i.e., is smaller than that calculated according to the formula, which indicates instability of the compound at this concentration of solution.

On the whole, the minimum for molecular electroconductivity in solutions with low D_p, correspond as a rule to a monomolecular state of the electrolyte.

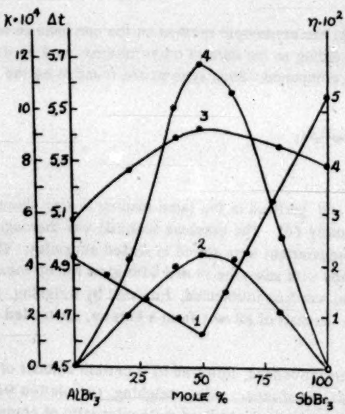

Fig. 1. Relation of freezing point lowering to $AlBr_3$ and $SbBr_3$ content (Curve 1), specific electroconductivity (Curve 2), viscosity Curve 3), and electroconductivity, corrected for viscosity, of the $SbBr_3-AlBr_3-C_2H_4Br_2$ system (Curve 4).

For calculation of the instability constant of a complex, several determinations of Δt should be carried out at isomolecular concentration, in which case the electroconductivity can be ignored, and the apparent molecular weight will be lower than that corresponding to the formula $SbBr_3 \cdot AlBr_3$. The instability constant in the given case is expressed by an equation, which is analogous to the thermal dissociation constant

$$SbBr_3 \cdot AlBr_3 \rightleftharpoons SbBr_3 + AlBr_3; \quad K = \frac{a^2 \cdot C}{1-a}.$$

The degree of decomposition is determined by the expressions $\left(\frac{\Delta t'}{\Delta t} - 1\right)$, where $\Delta t'$ = lowering of the freezing point of the solution, determined experimentally; Δt = theoretically calculated freezing temperature of the solution, under conditions in which the complex is not dissociated, under the author's conditions the constant being equal to 0.01238, a = 0.389. This provides the opportunity for evaluating the degree of stability of the complex under the given conditions.

The $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$ system

Aluminum halide ethers as electrolytes have frequently attracted the attention of investigators [12]. Up to the present time, however, it has not been determined whether $AlBr_3$ forms only one complex compound with $(C_2H_5)_2O$, or more. According to the thermal analysis data, the presence of one compound $AlBr_3 \cdot (C_2H_5)_2O$ has been established, but the system has not been studied over the entire range of concentrations [13].

The investigational procedure used by the author for interaction between two substances in a third indifferent solvent provides an opportunity for observing changes of one or more properties over the entire range of concentrations of the $AlBr_3$ and $(C_2H_5)_2O$ components.

The given system was investigated by the authors through conductivity and by the cryoscopic method. The results of electroconductivity measurements are compiled in Table 2; cryoscopic data are presented graphically.

TABLE 2

Mole ratio $\frac{AlBr_3 + (C_2H_5)_2O}{C_2H_4Br_2} = 0.05$ Temperature 20°

$AlBr_3$ (in mole %)	$\kappa \cdot 10^5$	$AlBr_3$ (in mole %)	$\kappa \cdot 10^5$	$AlBr_3$ (in mole %)	$\kappa \cdot 10^5$
0	-	48.76	3.12	71.60	0.29
21.35	0.82	50.75	1.09	79.10	0.26
26.09	1.04	52.58	0.20	100	-
38.04	2.32	62.66	0.38	-	-
41.78	2.41	69.49	0.37	-	-

It follows from the electroconductivity data that aluminum bromide forms two compounds with ether, of the compositions $AlBr_3 \cdot (C_2H_5)_2O$ and $2AlBr_3 \cdot (C_2H_5)_2O$. The sharp decrease in electroconductivity after reaching a maximum is evidently affected by a shifting of the equilibrium to the side of formation of the $2AlBr_3 \cdot (C_2H_5)_2O$ complex, which is a poor conductor of the electric current.

As can be seen from Fig. 2, for this sytem, as well as for the preceding, the slightest decrease in freezing temperature corresponds to equimolecular composition of $AlBr_3 \cdot (C_2H_5)_2O$ compound. Consequently, the cryoscopic method brings to light quite readily one compound of the liquid phase. A certain scattering of the points is apparently caused by volatility of the ether.

It should be mentioned that the color of the solution changes upon transition from the predominating concentration of $AlBr_3$ to a predominating concentration of ether, from light yellow to colorless.

EVALUATION OF RESULTS

Upon investigating the electroconductivity of ternary systems under conditions of constant ratio of two components and variable concentration of the third, quite frequently the conductivity maxima do not correspond to the composition of the compound forming in the solution. Thus, for example, on the basis of an electroconductivity maximum for the system $SbBr_3-AlBr_3-C_6H_6$, a conclusion was made that in the solution a compound of the composition $SbBr_3 \cdot Al_2Br_6$ [14] is formed.

The author has demonstrated that the maximum disappears if viscosity is taken into account [11]. It should be mentioned that the composition of the compound in the concentrated solution can be determined, usually, by taking viscosity into account. The method used by the authors provides an opportunity for investigating any change in property over the entire concentration range for two components, with constant concentration of the third component, the indifferent solvent, and for working with small amouns of substances.

The advantage of this method lies in the fact that interaction of the substances with limited solubility at low temperature can be investigated, which in turn provides an opportunity for avoiding thermal decomposition. This method, however, is not without shortcomings. The principal disadvantage is that the third component (solvent) must be indifferent with respect to the other two components which is not always easy to select. Investigation of lowering in the freezing point of solutions, in contrast to other properties (electroconductivity, viscosity, surface tension, and others) differs also in the fact that the applicability of the method is conditioned by concentration of the components. The cryoscopic method is applicable to solutions of such concentration that, upon crystallization, only solvent separates in the solid phase. Comparison of data on various properties for the $SbBr_3-AlBr_3-C_2H_4Br_2$ system, studied at isomolar concentrations of 0.1 and 0.4, has indicated that the complex $SbBr_3 \cdot AlBr_3$ is the electrolyte in the given system. But the system $AlBr_3-(C_2H_5)_2O-C_2H_4Br_2$ which was investigated indicated that, according to conductivity, two compounds, $AlBr_3 \cdot (C_2H_5)_2O$ and $2AlBr_3 \cdot (C_2H_5)_2O$, are formed in the system, and according to cryoscopic data that only one compound $AlBr_3 \cdot (C_2H_5)_2O$ is formed. This fact, however, does not enable us to claim that the cryoscopic method provides an opportunity for detecting in the liquid phase only one compound.

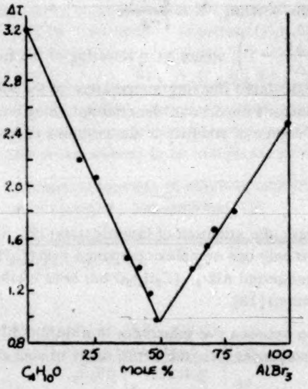

Fig. 2. Relation of freezing point lowering to composition for the $AlBr_2-(C_2H_5)_2O-C_2H_4Br_2$ system.

$$\frac{M_{AlBr_3} + M_{C_4H_{10}O}}{M_{C_2H_4Br_2}} = 0.05.$$

SUMMARY

1. The interaction of $AlBr_3$ with $SbBr_3$ in ethylene bromide as solvent has been studied by the cryoscopic method, and $AlBr_3$ with $(C_2H_5)_2O$ in the same solvent, by the cryoscopic method and by electroconductivity over the entire range of concentration.

2. It has been established that in the $SbBr_3-AlBr_3-C_2H_4Br_2$ system, the $SbBr_3 \cdot AlBr_3$ complex is the electrolyte. The instability constant has been calculated for the compound from cryoscopic data.

3. Two compounds, $AlBr_3 \cdot (C_2H_5)_2O$ and $2AlBr_3 \cdot (C_2H_5)_2O$, are formed in the system $AlBr_3-(C_2H_5)_2O-C_2H_4Br_2$, according to electroconductivity data, and one compound, $AlBr_3 \cdot (C_2H_5)_2O$, according to cryoscopic data.

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INTERRELATIONSHIPS OF LITHIUM, SODIUM AND POTASSIUM SULFATES IN MELTS

THE TERNARY SYSTEM OF LITHIUM, SODIUM AND POTASSIUM SULFATES

E. K. Akopov and A. G. Bergman

In the D. I. Mendeleev system, in the first four groups, the first representative of the main group (2nd horizontal series) displays properties transitional to the element of the next group in the 3rd row, and it is only the second or third representative which fully reveals the characteristic properties of its group.

Lithium, being the leading element of the first main subgroup of the periodic system, occupies a special position with respect to the other alkali metals. This peculiarity consists in the fact that in its properties lithium salts in many ways resemble compounds of the alkaline earth metals, and magnesium above all, For example, lithium and magnesium salts do not give a compound with the common anion; they crystallize from melts either in the form of a continuous series of solid solutions, or they represent systems with a simple eutectic. This characteristic of lithium, distinct from its analogs – the alkali metals – is revealed by the fact that its salts have a tendency to form compounds with salts of the other alkali metals. Among the lithium salts, its sulfate has a clear-cut ability to form complexes with sulfates of the alkali metals.

Investigations by the authors have demonstrated that lithium, sodium and potassium sulfates, though among the simplest of inorganic salts, display extremely complex chemical interrelationships in melts: they form among themselves complex compounds of the double salt type, as well as ternary salts.

The interrelationships of lithium, sodium and potassium sulfates have been investigated for the first time by the present authors, in the form of a ternary system, on the basis of a prism of the composition of a reciprocal quaternary system composed of the chlorides and sulfates of lithium, sodium and potassium, [illegible]

EXPERIMENTAL

Investigation was carried out in a platinum crucible with platinum stirrer, by the visual polythermal method. Temperature of appearance of the first cyrstals was measured by means of a Pt-Rh–Au-Pd-Pt thermocouple, 0.5 mm in diameter, and a millivoltmeter.

The initial chemically pure salts were recrystallized twice. The melting points adopted for lithium, sodium and potassium sulfates were, respectively, 856, 884 and 1069°. All compositions are expressed in molecular percentage.

Investigation of the given sytem was attended with great difficulties. Since the sulfates of the given elements crystallize poorly from melts, and in several areas of the system there occurs glass formation and gelling, and since supercooling frequently took place, determination of the start of crystallization presented formidable difficulties. As indicated from the authors' experiments deviation in the melting point of the composition at cross-sectional points of the internal part fluctuated within the range of 1%, which satisfies the requirements pertaining to accuracy of determination.

Binary Systems

1. Li_2SO_4–Na_2SO_4 was investigated by R. Nacken [1] through the use of heating and cooling curves, followed by other investigators using the thermographic method, and also the visual polythermal method, the latter method being used by the present authors.

The authors' data for the liquidus curve deviate considerably from the data of R. Nacken. According to the authors' data, lithium and sodium sulfates form two compounds melting with decomposition, of the composition 1:1

$Li_2SO_4 \cdot Na_2SO_4$ and 1 : 2 ($Li_2SO_4 \cdot 2Na_2SO_4$).

In Fig. 1 (according to the data of Table 1), the liquidus diagram for $Li_2SO_4-NaSO_4$ is given. It consists of four crystallization branches: Na_2SO_4 compounds 1 : 1, 1 : 2 and α-Li_2SO_4, which intersect at 637° and 62.5% Na_2SO_4, at 620° and 48% Na_2SO_4, and at 596° and 36.5% Na_2SO_4, respectively.

2. $Li_2SO_4-K_2SO_4$ was investigated by R. Nacken [1] and other investigatiors, the present authors included.

Lithium and potassium sulfates form a stable compound of the composition 1 : 1, with a melting point of 732°. The authors have also established formation of a second compound, melting with decomposition, of the composition 2 : 1 ($2Li_2SO_4 \cdot K_2SO_4$) with m.p. 550°; it can be called "lithium langbeinite".

The liquidus diagram for the system $Li_2SO_4-K_2SO_4$ (Fig. 1) consists of five branches: $\alpha/\beta = Li_2SO_4$, compounds 2 : 1, 1 : 1, and K_2SO_4.

The heteromorphic transformation point of Li_2SO_4 is at 572° and 83% Li_2SO_4. Eutectic points at 532° and 81% Li_2SO_4, and at 712° and 39.5% Li_2SO_4; transitional point at 550° and 76.5% Li_2SO_4, maximum at 732° and 50% Li_2SO_4.

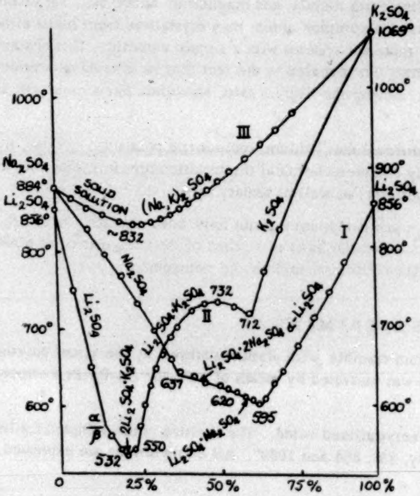

Fig. 1. Auxiliary binary systems of the ternary system, Li, Na, K‖SO_4.
I = Lithium and sodium sulfates;
II = lithium and potassium sulfates;
III = sodium and potassium sulfates;

$Na_2SO_4-K_2SO_4$ was investigated by Nacken [1], Jänecke [2], and the present authors. Sodium and potassium sulfate form a continuous series of solid solutions, with a minimum, according to Nacken, at 830° and 20% K_2SO_4, and according to Jänecke, 845° and 23.5% K_2SO_4, and according to the authors's data, at 832° and 25% K_2SO_4. According to the data of the first two authors, solid solutions below the liquidus line decompose, and the components convert into another crystalline modification (rhomboidal), Na_2SO_4 at 232° and K_2SO_4 at 590° according to Nacken, and 225 and 587°, respectively, according to Jänecke. Moreover, at 476° the solid solutions decompose with formation of a compound of the composition 1 : 1, which forms organic solid solutions with its components.

In Fig. 1 (according to the data of Table 1) a diagram for melting of the system $Na_2SO_4-K_2SO_4$, according to the authors' data, is given.

Internal Sections

20 internal sections were studied (Figs. 2,3 and 4, Tables 2,3,4,5); the general characteristics for these profiles are given in Table 6.

TABLE 1

Binary Systems

$Li_2SO_4-Na_2SO_4$				$Li_2SO_4-K_2SO_4$				$Na_2SO_4-K_2SO_4$			
Li_2SO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature
0	884°	55	616°	0	856°	32	666°	0	884°	42	858°
10	828	58	611	5	750	35	688	5	870	45	868
15	796	60	608	10	650	32	702	10	856	48	876
20	768	62	604	15	556	42	722	15	848	51	886
25	700	64	608	18	542	46	730	20	836	55	900
30	696	67	628	20	536	50	732	24	833	60	915
35	660	70	644	22	542	55	726	27	832	65	932
38	644	75	676	24	574	60	716	30	836	70	950
42	636	80	712	26	600	65	770	33	841	75	970
45	628	85	744	28	625	70	825	36	846	100	1069
50	626	90	782	30	648	100	1069	39	852	-	-
52	620	100	856	-	-	-	-	-	-	-	-

TABLE 2

A – Li_2SO_4 (in %)

Section I				Section II				Section VI			
A	Temperature	A	Temperature	A	Temperature	A	Temperature	A	Temperature	A	Temperature
0	846°	42	624°	0	834°	34	644°	0	912°	30	700°
5	812	46	616	5	798	36	636	5	876	34	686
10	786	50	606	10	770	38	628	10	842	38	667
15	750	54	600	15	742	40	624	12	820	42	673
20	724	58	596	18	722	42	614	15	796	46	670
25	690	62	590	22	690	45	611	18	770	50	660
30	660	66	580	25	674	48	608	21	748	52	654
34	640	70	578	30	654	50	606	24	732	55	640
38	632	75	625					27	718	58	632

A full projection is given in Fig. 5 for the melting diagram of Li, Na, K|| SO_4 system on on a composition triangle, where the isotherms are drawn at every 50°, and one at 25° (indicated by the broken line).

Of special interest are the internal phases, symbolized by the letters [A] and [B]. This section of the diagram was investigated in more detail by the authors; although the crystallization fields for phases [A] and [B] pass through 14 internal sections (Fig. 4), their crystallization branches are clearly defined on the curves.

In addition, the authors investigated four internal sections through the quaternary reciprocal prism system of Li, Na, K||Cl, SO_4 composition, whose diagrams completely confirmed the reality of the [A] and [B] phases.

Lithium sulfate is found to be a good complex former in melts: with sodium and potassium sulfates it forms two compounds, respectively. It is quite understandable that these sulfates also form compounds inside the system. Sodium and potassium sulfates give a compound of the composition 1 : 1, but the maximum temperature for its existence is lower than the formation temperature of the internal phases [A] and [B]. Moreover, in the reciprocal system Na, K||Cl, SO_4 ivesstigated by the authors, solid solutions below 706° decompose with formation of an independent phase [X]; but the configuration for the prism of phase [X] composition does not border on the [A] phase, and it should therefore be assumed that they are ternary complex compounds, highly dissociated, and possibly forming solid solutions with the components.

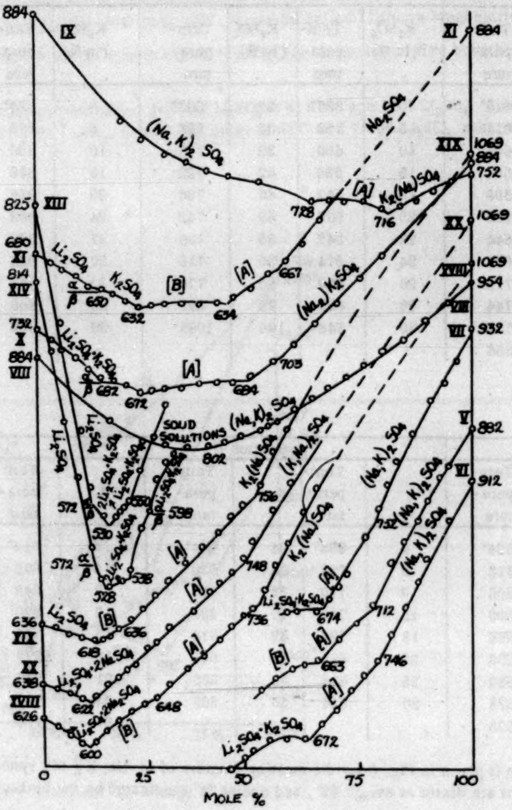

Fig. 2. Internal sections of Li, Na, K||SO$_4$ system
[A] and [B] - internal phases of the system, obscure in composition

A projection of the crystallization pattern on the side of $Na_2SO_4-K_2SO_4$ is given in Fig. 6, by means of which the monovariant crystallization curves are located, as well as the non-variant ternary points, among which 1 is eutectic and 9 are transitional.

Triangulation of the system, however (Fig. 7) is complicated since the [illegible] accurate compositions for the internal phases [A] and [B] (compounds) are not known; they were arbitrarily selected by the authors.

The sides of the phase triangles are indicated by the continuous lines, which were obtained on the basis of known compositions for the compound on the side; the broken lines of the phase triangle result from triangulation on the basis of internal compounds, whose compositions are taken tentatively. Arrows indicate position of the non-variant point for the correspondnig phase triangles.

TABLE 3

A - Li_2SO_4, B - K_2SO_4 (in %)

Cross section V		Cross section VII		Cross section XIII		Cross section XIV		Cross section XVII	
A	Temp.	A	Temp.	B	Temp.	B	Temp.	B	Temp.
-	882°	-	932°	-	825°	-	814°	-	616°
5	846	3	902	5	714	3	752	3	602
10	814	6	884	10	618	6	686	6	596
12	796	9	866	12	564	9	634	9	590
15	776	13	836	15	588	12	568	15	596
18	758	16	810	18	536	14	538	21	619
22	718	18	788	19	542	16	530	24	630
26	700	21	766	20	547	18	535	27	640
30	826	24	740	21	550	21	546	-	-
35	662	28	705	22	555	24	586	-	-
38	662	30	694	24	580	26	602	-	-
41	657	32	680	27	640	28	632	-	-
45	648	35	673	30	660	30	648	-	-
48	636	40	670	-	-	32	658	-	-
-	-	42	672	-	-	-	-	-	-

TABLE 4

A - Li_2SO_4, B - K_2SO_4, C - Na_2SO_4 (in %)

Cross section III		Cross section IV		Cross Section X		Cross section XV		Cross section XVII		Cross section XX	
A	Temp.	A	Temp.	C	Temp.	B	Temp.	B	Temp.	B	Temp.
0	834°	0	858°	0	732°	0	782°	0	626°	0	638°
5	802	3	842	3	723	2	720	3	618	3	634
10	776	6	818	6	712	4	670	6	612	6	630
14	754	9	798	9	705	6	630	9	604	9	625
18	730	12	782	12	696	9	564	12	603	12	628
20	718	15	756	15	688	12	514	15	615	15	638
24	692	18	740	18	685	14	522	18	624	18	647
26	682	21	720	21	680	16	532	21	632	20	653
28	670	24	698	24	674	18	540	24	640	22	658
32	654	27	680	27	674	20	540	27	648	25	674
34	644	30	672	30	676	22	550	30	660	28	678
36	634	33	660	34	678	24	566	34	674	30	694
38	630	36	648	38	680	26	584	38	686	36	708
42	620	38	648	42	682	28	620	42	702	40	728
45	614	40	646	46	684	30	634	45	715	42	735
48	605	42	644	50	688	32	634	48	726	45	746
51	597	45	637	55	702	34	674	50	732	48	760
55	588	48	627	60	716	39	692	52	750	50	775
58	584	52	615	65	735	42	700	55	774	52	780
62	576	56	590	70	754	45	708	58	794	55	805
65	570	60	578	75	778	50	712	62	824	58	831
68	564	64	574	80	798	55	704	65	846	62	852
72	558	68	566	100	884	60	716				
75	550					63	740				
77	578										

TABLE 5

B - K_2SO_4, C - Na_2SO_4 (in %)

Cross section VIII		Cross section IX		Cross section XI		Cross section XII		Cross section XVI		Cross section XIX	
C	Temp.	C	Temp.	C	Temp.	C	Temp.	B	Temp.	B	Temp.
0	954*	0	752*	0	680*	0	560*	0	748*	0	636*
10	918	5	746	3	673	3	542	3	624	3	632
15	902	10	736	6	666	6	525	8	549	6	626
20	890	15	728	9	660	9	538	15	556	9	622
24	876	20	717	12	651	12	548	16	558	12	620
28	866	24	721	15	648	15	552	18	562	14	620
32	856	26	728	18	645	18	560	21	568	16	624
36	848	28	728	21	638	21	567	24	600	18	630
40	836	32	730	24	631	25	575	26	615	21	640
44	824	36	728	27	634	30	586	28	632	24	650
46	822	40	736	30	634	34	594	30	646	27	662
48	818	48	746	34	635	38	602	32	656	30	678
52	818	55	752	38	634	42	608	35	670	34	694
56	808	60	757	42	635	46	616	38	678	38	708
60	804	65	766	46	639	50	626	42	680	42	722
65	802	70	774	50	648	52	628	45	696	45	738
75	806	75	788	54	662	55	632	50	698	48	748
83	826	80	804	58	674	58	636	55	694	52	778
100	884	100	884	62	690	62	660	58	716	55	798
-	-	-	-	66	712	66	683	62	764	58	818
-	-	-	-	-	-	70	708	-	-	-	-

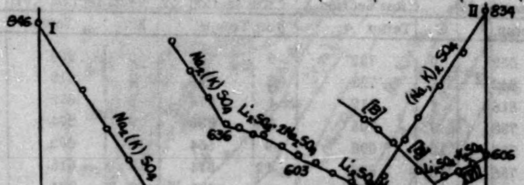

Fig. 3. Internal sections of the Li, Na, K ‖ SO_4 system.
[A] and [B] = internal sections of the phase with obscure composition.

TABLE 6

$(Na, K)_2SO_4$ — continuous series of solid solutions of sodium and potassium sulfates $Na_2(K)SO_4$ and $K_2(Na)SO_4$ — sulfates of the same elements resulting from decomposition of the solid solutions. $D = Li_2SO_4 \cdot K_2SO_4$; $G = 2Li_2SO_4 \cdot K_2SO_4$; $D_1 = Li_2SO_4 \cdot Na_2SO_4$; $D_2 = Li_2SO_4 \cdot 2Na_2SO_4$

Section number	Initial mixture of components (in %)	Component added	Branches of the crystallization curves and their cross sections												
			I	Crossection		II	Crossection		III	Crossection		IV	Crossection		V
				(in %) *	Temperature		(in %) *	Temperature		(in %) *	Temperature		(in %) *	Temperature	
I	$15K_2SO_4 + 85Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	32.5	638°	D_2	50.5	606°	D_1	62.5	573°	α-Li_2SO_4			
II	$22K_2SO_4 + 78Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	28.0	660	[A]	38.0	625	[C]						
III	$30K_2SO_4 + 70Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	25.5	675	[A]	36.0	633	[C]	56.5	582	D_1	75.0	550°	Li_2SO_4
IV	$42K_2SO_4 + 58Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	25.0	694	[A]	36.5	648	[C]	57.0	580	D_1			
V	$50K_2SO_4 + 50Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	23.0	712	[A]	35.5	663	[C]						
VI	$59K_2SO_4 + 41Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	21.5	746	[A]	36.5	672	β-D						
VII	$65K_2SO_4 + 35Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	22.0	752	[A]	33.5	674	β-D						
VIII	$85K_2SO_4 + 15Li_2SO_4$	Na_2SO_4	Solid p – p $(Na, K)_2SO_4$ minimum at 802												
IX	$65K_2SO_4 + 35Li_2SO_4$	Na_2SO_4	$K_2(Na)SO_4$	18.5	716	[A]	35.0	728	$(Na, K)_2SO_4$						
X	$50K_2SO_4 + 50Li_2SO_4$	Na_2SO_4	α-D	16.0	682	β-D	25.5	672	[A]	49.0	684	$Na_2(K)SO_4$	56.0	703	$(Na, K)_2SO_4$
XI	$35K_2SO_4 + 65Li_2SO_4$	Na_2SO_4	α-D	13.0	650	β-D	24.0	632	[C]	45.0	634	[A]	56.0	663	$(Na, K)_2SO_4$
XII	$15K_2SO_4 + 85Li_2SO_4$	Na_2SO_4	β-Li_2SO_4	6.0	524	D_1	41.0	603	D_2	59.0	636	$Na_2(K)SO_4$			
XIII	$3Na_2SO_4 + 97Li_2SO_4$	K_2SO_4	α-Li_2SO_4	12.5	572	β-Li_2SO_4	16.5	530	G	28.5	550	α-D			
XIV	$5Na_2SO_4 + 95Li_2SO_4$	K_2SO_4	α-Li_2SO_4	12.5	572	β-Li_2SO_4	15.0	528	G	21.0	538	β-D	25.5	598	α-D
XV	$10Na_2SO_4 + 90Li_2SO_4$	K_2SO_4	α-Li_2SO_4	8.0	572	β-Li_2SO_4	12.0	514	G	21.0	546	β-D	26.5	594	α-D
XVI	$20Na_2SO_4 + 80Li_2SO_4$	K_2SO_4	α-Li_2SO_4	4.0	572	β-Li_2SO_4	8.0	548	G_1	21.5	565	β-D	56.5	690	$K_2(Na)SO_4$
XVII	$40Na_2SO_4 + 60Li_2SO_4$	K_2SO_4	D_1	11.5	584	[C]									
XVIII	$50Na_2SO_4 + 50Li_2SO_4$	K_2SO_4	D_2	11.0	600	[C]	27.0	648	[A]	51.0	736	$K_2(Na)SO_4$			
XIX	$55Na_2SO_4 + 45Li_2SO_4$	K_2SO_4	D_2	11.5	618	[C]	20.5	636	[A]	50.5	756	$K_2(Na)SO_4$			
XX	$60Na_2SO_4 + 40Li_2SO_4$	K_2SO_4	D_2	11.0	622	[A]	46.5	748	$K_2(Na)SO_4$						

---

* Percent of added component.

TABLE 7

No.	Name of the phase triangle	Ternary point	Temperature	Composition of ternary point (in mole%)		
				Li_2SO_4	Na_2SO_4	K_2SO_4
1	$2Li_2SO_4 \cdot K_2SO_4 - Li_2SO_4 - Li_2SO_4 \cdot Na_2SO$	E	512*	79.0	9.	12
2	$2Li_2SO_4 \cdot K_2SO_4 - Li_2SO_4 \cdot K_2SO_4 - Na_2SO_4$	P_1	536	73.0	6.5	20.5
3	$Li_2SO_4 \cdot K_2SO_4 - [B] - Li_2SO_4 \cdot Na_2SO_4$	P_2	568	58.0	19.25	22.75
4	$Li_2SO_4 \cdot Na_2SO_4 - [B] - Li_2SO_4 \cdot 2Na_2SO_4$	P_3	586	48.0	41.5	10.5
5	$[A] - [B] - Li_2SO_4 \cdot 2Na_2SO_4$	P_4	620	38.0	50.5	11.5
6	$[A] - Li_2SO_4 \cdot 2Na_2SO_4 - Na_2SO_4$	P_5	633	29.0	62.0	9.0
7	$[A] - (2Na_2SO_4 \cdot K_2SO_4) - Na_2SO_4$	P_6	668	25.0	56.0	19.0
8	$Li_2SO_4 \cdot K_2SO_4 - [A] - [B]$	P_7	667	38.0	25.5	36.5
9	$[A] - (2Na_2SO_4 \cdot K_2SO_4) - K_2SO_4$	P_8	756	34.0	10.5	55.5
10	$Li_2SO_4 \cdot K_2SO_4 - [A] - K_2SO_4$	P_9	682	20.5	29.5	50.0

* E , ternary eutectic point, P, ternary transitional point

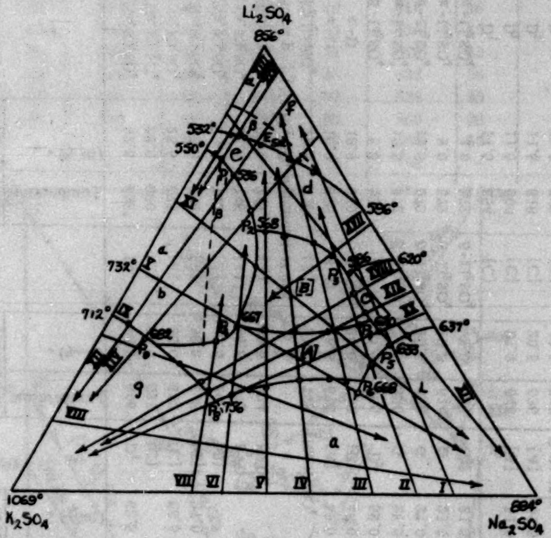

Fig. 4. Scheme of arrangement of internal sections for the system Li, Na, K || SO_4.
a) solid solutions $(Na,K)_2SO_4$, b) $Li_2SO_4 \cdot K_2SO_4$, c) $Li_2SO_4 \cdot 2Na_2SO_4$, d) $Li_2SO_4 \cdot Na_2SO_4$, e) $2Li_2SO_4 \cdot K_2SO_4$, f) α/β-Li_2SO_4, g) $K_2(Na)SO_4$ h) $Na_2(K)SO_4$.

It can be seen in Fig. 7 that the primary triangle of Li, Na, K || SO_4 system is broken up into 10 phase (secondary) triangles, which are given in Table 7.

The diagram for crystallization surface of the system consists of 10 areas, among which two correspond to heteromorphic modifications in Li_2SO_4 with a transition point at 572° and two homomorphic modifications for the compound $Li_2SO_4 \cdot K_2SO_4$, whose transition between themselves in the given system occurs within the interval of 555-670° (according to the branched projection, Fig. 6). The area occupied by each field in relation to the area of the triangle of compositions, is given in Table 8.

It should be indicated that the courses of the isotherms differ noticeably from one another in the internal planes. In the crystallization field of solid solutions $(Na,K)_2SO_4$, the isotherms 750-800° are characterized by considerable concavity toward $Na_2SO_4-K_2SO_4$. Moreover, in this area two monovariant curves radiate out from the two ternary points (p_8 and p_9), indicated by the broken line.

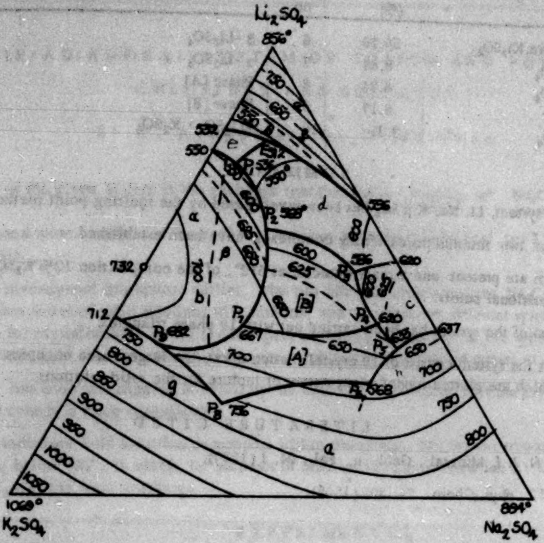
Li_2SO_4
856°
532
550
e
E
P_1
d
P_2 528°
596
a
β
b
732
712
P_9 682
P_7
[B]
[A]
P_4
P_5
P_3
P_6 568
P_8 756
620
637
680
667
g
h
c
a
1068°
K_2SO_4
884°
Na_2SO_4

Fig. 5. Projection of the melting diagram for the ternary system Li, Na, K || SO_4 in the composition triangle.
a) solid solutions $(Na,K)_2SO_4$ b) $Li_2SO_4 \cdot K_2SO_4$, c) $Li_2SO_4 \cdot 2Na_2SO_4$, d) $Li_2SO_4 \cdot Na_2SO_4$, e) $2Li_2SO_4 \cdot K_2SO_4$, f) α /β -Li_2SO_4, g) $K_2(Na)SO_4$, h) $Na_2(K)SO_4$. [A] and [B] = internal phases of obscure composition

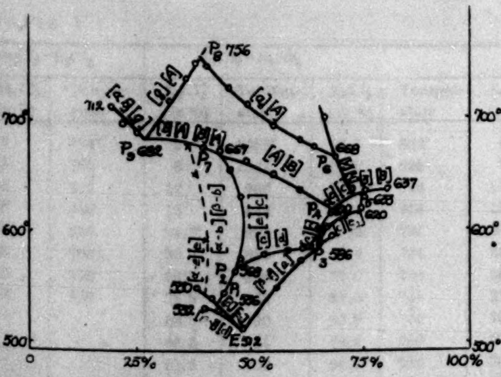

Fig. 6. Projection of the ternary system at one side of the triangle $Na_2SO_4-K_2SO_4$.
[A] and [B] = internal phases of obscure composition.
The other symbols same as in Fig. 5.

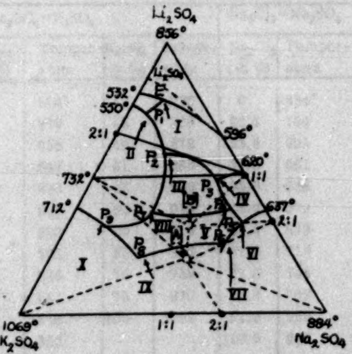
Li_2SO_4
856°
532°
550°
E
P_1
I
596°
2:1
II
P_2
680°
1:1
732°
III
P_3
IV
637°
712°
P_9
V
2:1
VIII
VI
P_8
I
IX
VII
1069°
K_2SO_4
1:1
2:1
884°
Na_2SO_4

Fig. 7. Triangulation scheme for the ternary system.
Explanation in text of Table 7.

TABLE 8

Field no.	Name of area of crystallization	Contained (%)	Field no.	Name of area of crystallization	Contained (%)
1	Solid solution $(Na,K)_2SO_4$	50.10	6	β-Li_2SO_4	1.30
2	α-$Li_2SO_4 \cdot K_2SO_4$	8.84	7	α-Li_2SO_4	4.36
3	β-$Li_2SO_4 \cdot K_2SO_4$	6.34	8	Phase [A]	8.85
4	$Li_2SO_4 \cdot Na_2SO_4$	8.17	9	Phase [B]	7.70
5	$Li_2SO_4 \cdot 2Na_2SO_4$	3.31	10	$2Li_2SO_4 \cdot K_2SO_4$	1.03

SUMMARY

1. The ternary system, Li, Na, K || SO_4 has been investigated by the melting point method.

2. In the system two internal phases, ternary complexes, have been established.

3. In the system are present one ternary eutectic at 512°, of the composition 12% K_2SO_4, 9% Na_2SO_4 and 79% Li_2SO_4, and 9 triple transitional points.

4. Triangulation of the system has been carried out with 10 phase triangles.

5. Diagrams for the system consist of 10 crystallization areas; the largest area occupies the field of solid solution $(Na, K)_2SO_4$, in which are plotted monovariant curves of rupture for the solid solutions.

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REVERSIBLE-ADIAGONAL SYSTEM OF SODIUM AND POTASSIUM-CHLORIDES AND SULFATES

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At the base of the given system is the exchange reaction $\underset{208.34}{K_2Cl_2} + \underset{332.33}{Na_2SO_4} \rightleftharpoons \underset{199.68}{Na_2Cl_2} + \underset{341.8}{K_2SO_4}$.

The conditional thermal effect of the exchange reaction amounts to 0.38 kcal per 1 gram equiv. toward the side Na_2Cl_2 + K_2SO_4.

Jänecke [1] investigated this system earlier. The two different binary systems $Na_2Cl_2-K_2Cl_2$ and $Na_2SO_4-K_2SO_4$ represent continuous series of solid solutions with minima, and the other two different systems are found to be eutectic. The diagram for crystallization points is composed, according to Jänecke, of two areas of sodium and potassium sulfates and chlorides solid solutions, which divide the combined crystallization curves at a minimum of 518°.

The system has been investigated in detail by the authors. It was found that the crystallization diagram for a given interrelated system is more complicated.

The above-indicated solid solutions decompose within the system, and the decomposition products of the sulfates form a phase below 706°, to which, for purposes of orientation, the composition 3 : 1 ($3NaSO_4 \cdot K_2SO_4$) or 2 : 1 ($2Na_2SO_4 \cdot K_2SO_4$) has been attributed.

EXPERIMENTAL

Investigation was carried out by the visual-polythermal method [2,3]. The initial salts, chemically pure, were recrystallized twice; the melting temperatures for sodium and potassium sulfates were adopted, respectively, as 884 and 1069°, and the chlorides as 800 and 774°.

In the work, only a portion of the investigated cross-sections and experimental points are given. All compositions are expressed as molecular percentage.

TABLE 1

$Na_2Cl_2-K_2Cl_2$		$K_2Cl_2-K_2SO_4$				$Na_2SO_4-K_2SO_4$				$Na_2Cl_2-Na_2SO_4$	
Na_2Cl_2 (in %)	Temperature	K_2Cl_2 (in %)	Temperature	K_2Cl_2 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	Na_2Cl_2 (in %)	Temperature
0	774°	0	1069°	57.5	692°	0	884°	42	858°	0	884°
15	760	6	1026	62.0	698	5	870	45	869	20.4	724
30	697	12	986	66.0	706	10	856	48	876	25.5	691
50	660	18	948	69.5	713	15	848	51	886	30.8	661
60	665	24.5	902	70.0	724	20	836	55	900	35.0	628
75	700	30.5	866	77.0	734	24	833	60	915	48.0	679
75	700	30.5	866	77.0	734	24	833	60	915	48.0	679
100	800	36.5	828	81.0	740	27	832	65	932	61.0	716
		42.5	790	85.0	750	30	836	70	950	71.3	748
		48.5	754	89.0	760	33	841	75	970	81.3	762
		51.5	732	94.5	770	36	846	100	1069	91.3	785
		54.5	713	100.0	774	39	852			100.0	800

Binary Systems. The liquidus curves for binary systems are shown in Fig. 1 (Table 1). 1. $Na_2Cl_2-K_2Cl_2$ – a continuous series of solid solutions with minimum at 658° and 50% of components; at lower temperature, the solid solutions decomposed below 500° (Figs. 1, IV [4]). 2. $Na_2SO_4-K_2SO_4$ – a continuous series of solid solutions with minimum at 25% K_2SO_4, and 832°;, the solid solutions decomposed at 476° to form a compound 1 : 1 [3] (Fig. 1,I).

3. $Na_2Cl_2-Na_2SO_4$ – eutectic at 35% Na_2Cl_2 and 628° [5] (Fig. 1, III). 4. $K_2Cl_2-K_2SO_4$ – a eutectic at 690° and 42% K_2SO_4 [1,6] (Fig. 1, II).

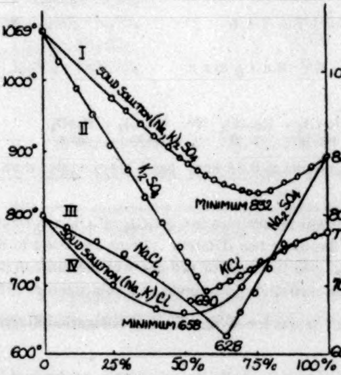


Fig. 1. Lateral binary systems.
I - $K_2SO_4-Na_2SO_4$, II - $K_2SO_4-K_2Cl_2$, III - $Na_2Cl_2-Na_2SO_4$,
IV - $Na_2Cl_2-K_2Cl_2$.

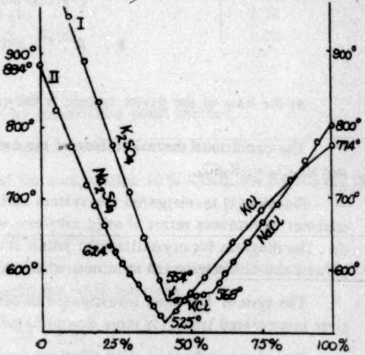


Fig. 2. Diagonal sections of the interrelated system.
I - $Na_2Cl_2-K_2SO_4$, II - $Na_2SO_4-K_2Cl_2$.

Diagonal Cross Sections. $Na_2Cl_2-K_2SO_4$, the unstable corss-section (Fig. 2, I, Table 2), consists of three branches K_2SO_4, KCl and NaCl, which intersect, respectively, at 57% K_2SO_4 and 554°, 41.5% K_2SO_4 and 568°. $K_2Cl_2-Na_2SO_4$ – an unstable section of the melting curve (Fig. 2, II, Table 2); it intersects the internal field phase. It consists of three branches: Na_2SO_4, [X], KCl, which cross at 624° and 24.6% K_2Cl_2 and at 525° and 41.5% K_2Cl_2.

Internal Sections.

16 internal sections (Figs. 3,4 and 5, Tables 3,4,5) were investigated. The characteristics of the sections are given in Table 6.

The internal field for the system, symbolized by "X", was investigated in detail. It is intersected by 10 internal sections, on which curves the crystallization branch is clearly outlined.

Area "X" is also revealed through the five internal interrelated system of lithium, sodium and potassium sulfates and chlorides. In addition, several sections through the prism were investigated, passing through the volume of the crystallization phase "X", for which curves the reality of this phase was confirmed.

The authors assume that the internal field "X" is the independent phase, a combination of sodium and potassium sulfates which are formed during decomposition of the solid solutions of the sulfates.

Formation temperature for the phase "X" lies within the range 514 to 706° (on the basis of the crystallization branches, Fig. 7), and the composition 1 : 1, which is formed during decomposition of the solid solutions in the binary system $Na_2SO_4-K_2SO_4$ at 476° and cannot, therefore, be attributed to it.

The composition of phase "X" was not determined by the authors; however, it is quite possible that it contains more sodium sulfate, to which was given the definitive composition $3Na_2SO_4 \cdot K_2SO_4$ ("antiglazerite"), or $2Na_2SO_4 \cdot K_2SO_4$, which is in accordance with triangulation of the system. There is given in Fig. 6 a full projection of the Na, K‖Cl, SO_4 system in diagram form, and in Fig. 7 a projection of its crystallization branches on the side toward the $Na_2SO_4-K_2SO_4$ square.

One triple eutectic and two transitional points can be found on the diagram; therefore, by triangulation, the square for the interrelated system should be divided into three phase triangles. To triangulate the system, it is necessary to know the composition of the internal phase "X", which is found to be a binary compound, for which the compositions 3 : 1, or 2 : 1, are satisfactory. The triangulated sections, therefore, will radiate from the lateral side of the $Na_2SO_4-K_2SO_4$, of composition 2 : 1 ($2Na_2SO_4 \cdot K_2SO_4$); they are directed toward the apices of NaCl and of KCl, and divide the square for the interrelated system into 3 phase triangles.

TABLE 2

Unstable Diagonal

$Na_2Cl_2-K_2SO_4$						$K_2Cl_2-Na_2SO_4$			
Na_2Cl_2 (in %)	temperature	Na_2Cl_2 (in %)	temperature	Na_2SO_4 (in %)	temperature	K_2Cl_2 (in %)	temperature	K_2Cl_2 (in %)	temperature
0	1069°	45	556°	70	638°	0	884°	33	578°
10	950	48	558	75	665	5	824	36	560
15	890	50	562	80	694	10	772	38	548
20	832	52	563	85	722	15	718	40	532
25	773	55	565	90	750	18	690	45	540
30	708	60	582	95	776	21	662	50	564
35	645	62	594	100	800	25	624	55	588
40	586	65	610			27	608	65	635
						30	594	70	682

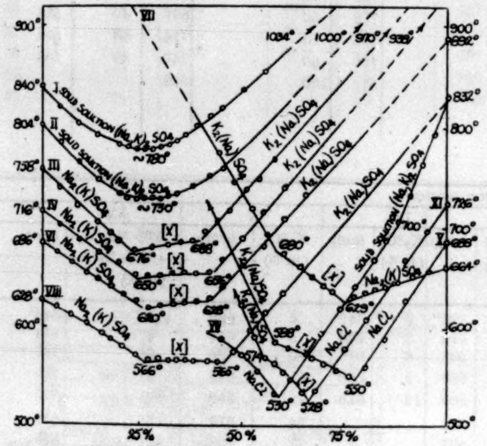


Fig. 3. Internal cross sections through the system. Roman numerals = cross section numbers, X = crystallization branch of the internal phase.

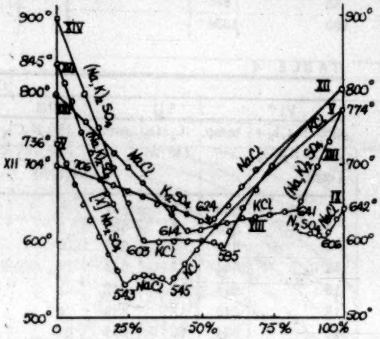


Fig. 4. Internal cross sections through the system. [X] = crystallization branch of internal phase.

I. $Na_2Cl_2-Na_2SO_4-2Na_2SO_4 \cdot K_2SO_4$ with a transition point at 534° and 13.5% Na_2Cl_2, 25.5% K_2Cl_2, 61% Na_2SO_4.

II. $Na_2Cl_2 + 2Na_2SO_4 \cdot K_2SO_4-K_2Cl_2$ with eutectic point at 514° and 2.5% Na_2Cl_2, 39% K_2Cl_2, 58.5% Na_2SO_4.

III. $K_2Cl_2-2Na_2SO_4 \cdot K_2SO_4-K_2SO_4$ with transition point at 538° and 41.5% K_2Cl_2, 53% Na_2SO_4, 5.5% K_2SO_4.

The diagonal sections do not participate in the triangulation; they are found to be unstable, which is also indicated by the transitional thermal effect for the given system; the latter, therefore, according to the classification [7], is found to be a reversibly adiagonal interrelated system. The diagram consists of three main areas of crystallization, among them two areas of solid solutions (Na, K)Cl and $(Na, K)_2SO_4$, of which the first decomposes within the system into the components, and the second with formation of an inner phase "X". The largest areas are occupied by solid solutions of chloride and their decomposition products,

Decomposition of solid solutions occurs on the basis of crystallization branches for the chlorides at 622° and for the sulfates at 706°.

TABLE 3

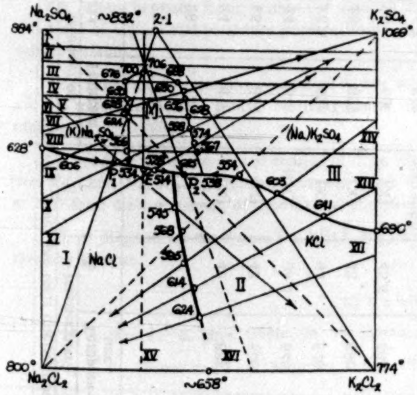
Cross section									
I		II		III		IV		V	
5% K_2Cl_2 + 95% K_2SO_4 (in %)	temp.	10% K_2Cl_2 + 90% K_2SO_4 (in %)	temp.	15% K_2Cl_2 + 85% K_2SO_4 (in %)	temp.	20% K_2Cl_2 + 80% K_2SO_4 (in %)	temp.	K_2Cl_2 (in %)	temp.
0	840°	0	804°	0	758°	0	716°	0	736°
5	820	5	784	5	740	5	702	3	705
10	804	10	764	10	724	10	688	6	678
15	794	15	748	15	706	15	674	9	652
20	783	20	733	18	696	20	664	12	630
22	782	22	730	20	687	24	653	15	608
24	780	24	730	24	678	27	650	18	586
26	780	26	730	28	681	30	652	21	564
28	780	28	731	32	684	33	653	24	542
30	781	30	731	35	686	36	654	27	554
32	784	32	732	38	688	39	655	30	558
34	788	34	735	41	696	42	658	33	556
36	794	36	738	44	708	45	668	36	554
39	802	38	742	48	718	50	690	40	556
42	812	42	752	50	732	55	714	44	573
45	820	45	760	54	750	60	740	49	590
50	837			58	570	100	938		
55	856								
100	1034								

TABLE 4

Cross section											
VI		VII		VIII		IX		X		XVI	
25% K_2Cl_2 + + 75% K_2SO_4 (in %)	temp.	K_2SO_4 (in %)	temp.	35% K_2Cl_2 + + 65% K_2SO_4 (in %)	temp.	K_2SO_4 (in %)	temp.	K_2SO_4 (in %)	temp.	37% Na_2Cl_2 + + 63% K_2Cl_2 (in %)	temp.
0	686°	0	664°	0	828°	0	642°	0	688°	0	841°
4	674	4	657	8	612	3	628	5	654	3	814
8	664	8	652	16	593	6	610	10	626	6	787
12	654	12	646	18	588	9	608	15	590	9	750
15	646	15	642	21	580	12	610	20	562	12	720
18	640	18	638	24	572			24	552	15	686
21	634	20	635	27	562			27	558	18	666
24	626	23	632	30	566			30	564	20	652
27	620	28	637	32	566			33	568		
30	621	30	643	34	565			36	574		
33	622	33	652	38	565			39	580		
36	624	36	661	41	564			42	584		
39	626	40	674	44	563			45	614		
42	628	44	694	48	580			50	654		
45	641	48	720	52	596			55	700		
50	662	52	748	56	618			60	740		
55	684	56	776	60	638			100	1069		
60	708	100	1069	65	658						
65	730			100	832						
100	892										

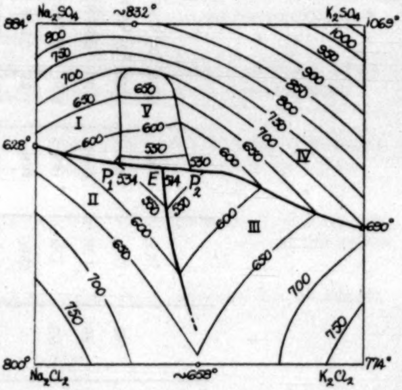
TABLE 5

Cross section									
XI		XII		XIII		XIV		XV	
K_2SO_4 (in %)	temp.	Na_2Cl_2 (in %)	temp.	Na_2Cl_2 (in %)	temp.	Na_2Cl_2 (in %)	temp.	30% K_2Cl_2 + + 70% $NaCl_2$ (in %)	temp.
0	726°	0	704°	0	774°	0	900°	0	832°
5	696	10	692	5	736	5	850	3	794
10	668	15	686	10	696	10	800	6	783
15	640	20	678	15	674	15	754	9	732
20	606	25	670	20	640	20	700	12	706
25	580	30	662	25	636	25	654	15	688
28	560	35	652	30	633	30	603	18	668
32	536	40	644	35	630	35	602	22	644
35	534	45	636	40	626	40	603	26	620
38	550	50	628	45	622	45	602	30	595
40	556	55	630	50	618	50	601	34	572
42	564	60	648	55	614	55	598	38	548
44	570	65	672	60	637	60	614	42	532
47	590	70	694	65	656	65	644	46	556
50	625	100	800	70	680	70	670	50	572
55	676			75	700	75	700	55	588
60	723			80	720				



Na_2SO_4
884°
~832°
2·1
K_2SO_4
1069°
628°
690°
800°
Na_2Cl_2
~658°
K_2Cl_2
774°
(K)Na_2SO_4
(Na)K_2SO_4
M
P_1
E
P_2
I
NaCl
II
III
KCl

Fig. 5. Placement scheme for internal sections. Roman numerals = number of cross section



Na_2SO_4
884°
~832°
K_2SO_4
1069°
628°
690°
800°
Na_2Cl_2
~658°
K_2Cl_2
774°
I
II
III
IV
V
P_1
E
P_2
534
514

Fig. 6. Projection of melting point diagram on composition square of the interrelated system. Crystallization fields: I - (K)Na_2SO_4, II - NaCl, III - KCl, IV - (Na)K_2SO_4.

TABLE 6

Cross section number	Initial mixture of components (in %)	Component being added to a mixture of the components (in %)	Branches of the crystallization curves and their intersections						
			I	Intersection		II	Intersection		III
				%*	Temperature		%	Temperature	
I	$5Na_2Cl_2 + 95Na_2SO_4$	$5K_2Cl_2 + 95K_2SO_4$	$(Na, K)_2SO_4$ minimum	27	780°				
II	$10Na_2Cl_2 + 90Na_2SO_4$	$10K_2Cl_2 + 90K_2SO_4$	$(Na, K)_2SO_4$ minimum	28	730				
III	$15Na_2Cl_2 + 85Na_2SO_4$	$15KCl + 85K_2SO_4$	$Na_2(K)SO_4$	24	676	[X]	40	688*	$K_2(Na)SO_4$
IV	$20Na_2Cl_2 + 80Na_2SO_4$	$20K_2Cl_2 + 80K_2SO_4$	$Na_2(K)SO_4$	25	650	[X]	42	656	$K_2(Na)SO_4$
V	$20Na_2Cl_2 + 80Na_2SO_4$	KCl	$Na_2(K)SO_4$	24	543	NaCl	38.5	545	KCl
VI	$25Na_2Cl_2 + 75Na_2SO_4$	$25K_2Cl_2 + 75K_2SO_4$	$Na_2(K)SO_4$	26.5	620	[X]	43	628	KCl
VII	$30Na_2Cl_2 + 70Na_2SO_4$	K_2SO_4	$Na_2(K)SO_4$	25	629	[X]	42	680	KCl
VIII	$35Na_2Cl_2 + 65Na_2SO_4$	$35KCl + 65K_2SO_4$	$Na_2(K)SO_4$	26	566	[X]	45.5	565	KCl
IX	$40Na_2Cl_2 + 60Na_2SO_4$	K2SO$_4$	NaCl	6.5	606	$Na_2(K)SO_4$			
X	$50Na_2Cl_2 + 50Na_2SO_4$	NaCl	NaCl	22.5	550	[X]	42.5	588	$K_2(Na)SO_4$
XI	$60Na_2Cl_2 + 40Na_2SO_4$	NaCl	NaCl	33.5	528	[X]	40.3	574	$K_2(Na)SO_4$
XII	$65K_2Cl_2 + 35K_2SO_4$	NaCl	KCl	53	624	NaCl			
XIII	$45K_2Cl_2 + 55K_2SO_4$	NaCl	$K_2(Na)SO_4$	16.5	641	KCl	55	614	NaCl
XIV	$25K_2Cl_2 + 75K_2SO_4$	NaCl	$K_2(Na)SO_4$	30	603	KCl	58	595	NaCl
XV	$70Na_2SO_4 + 30K_2SO_4$	$30K_2Cl_2 + 70Na_2Cl_2$	$(Na, K)_2SO_4$	12.5	700	[X]	36	530	NaCl
XVI	$28Na_2SO_4 + 72K_2SO_4$	$37K_2Cl_2 + 63Na_2Cl_2$	$(Na, K)_2SO_4$	12.5	706	[X]			

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* Percentage of component or of mixture added.

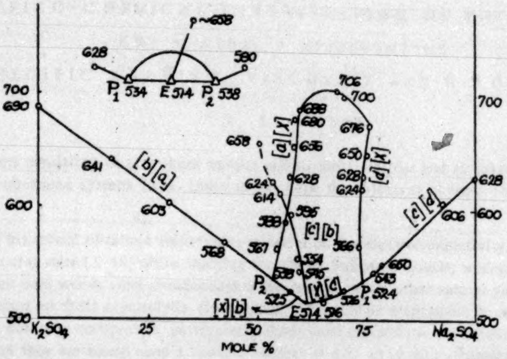

Fig. 7. Projection of crystallization branches of the interrelated system toward the square of compositions Na_2SO_4—K_2SO_4.
a = the solid solutions $(Na, K)_2SO_4$, b = KCl, c = NaCl, d = Na_2SO_4. "X" = internal phase of the system, E = eutectic, P_1 and P_2 = transition points

SUMMARY

1. The Na, K||Cl, SO_4 system, with a conditional thermal effect of 0.38 kcal per gram equiv. for the exchange reaction, toward $Na_2Cl_2 + K_2SO_4$, is found to be a reversible adiagonal interrelated system upon triangulation, starting from the pole of composition of the $2Na_2SO_4 \cdot K_2SO_4$ or the $3Na_2SO_4 \cdot K_2SO_4$. compound.

2. There has been found within the system a crystallization area of independent phase, found to be a binary compound of sodium and potassium sulfates, formed by decomposition of solid solutions of Na_2SO_4—K_2SO_4 binary system sulfates.

3. There are found in the system: one ternary eutectic point at 514° and 2.5% Na_2Cl_2, 39% K_2Cl_2, 58.5% Na_2SO_4 and two triple transitional points. By triangulation, the square for the interrelated system is divided into 3 phase triangles.

4. A diagram of the system consists of three major crystallization fields, amidst two continuous solid solutions, (Na, K)Cl and $(Na, K)_2SO_4$, which decompose within the system: chlorides at 622° form the components, and sulfates at 706° form the compounds, of hypothetical compositions 3 : 1 and 2 : 1.

5. A diagram for the system Na, K||Cl, SO_4, investigated by the authors, differs completely from the diagram given by Jänecke.

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Rostov-on-Don State University

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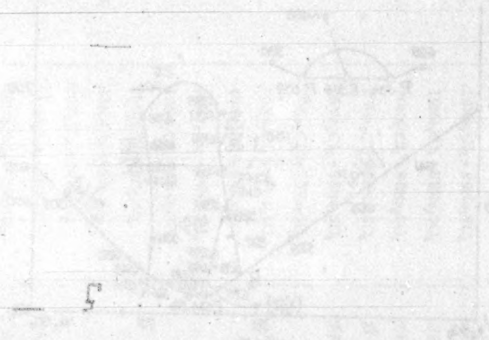

Fig. [illegible] of crystallization [illegible] of the intermediate system [illegible]

[illegible]

S U M M A R Y

1. The Na, K ∥ [illegible] system [illegible]

2. [illegible]

3. [illegible]

4. A diagram of the system [illegible]

5. A diagram for the system [illegible]

L I T E R A T U R E   C I T E D

1. E. Jänecke, Z. phys. Chem. [illegible]

2. [illegible] Alekseev and [illegible] Bergman, [illegible]

3. A. G. Bergman and I. N. Alekseev, [illegible]

4. N. S. Kurnakov and S. F. Zhemchuzhnyi, [illegible]

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7. A. G. Bergman and G. A. Bukhalova, [illegible]

Received August 31, 1962

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* Consultants Bureau Translation, p. 1498. ** Consultants Bureau Translation, p. [illegible]

PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM KBr – $AlBr_3$ – NITROBENZENE

(SPECIFIC GRAVITY, VISCOSITY AND CRYOSCOPY)

T. E. Koval

Ternary systems consisting of aluminum halides, alkali metal halides and an organic solvent, and in particular, the KBr · $AlBr_3$– nitrobenzene system, have, many times, been the objects of physico-chemical investigation of such anhydrous solutions.

Plotnikov and his school obtained voluminous material on the electroconductivity, electrolysis, decomposition potentials and molecular state [1-13] while studying the above-indicated system, wherein they gave data indicating formation of complex compounds from components of the system, while other authors gave the compositions of the complexes and schemes for their electrolytic dissociation. It should be mentioned, however, that deductions about the compositions of complex compounds, particularly about their electrolytic dissociations, are in many cases only hypothetical, because they are based upon a limited amount of data on physico-chemical properties.

In connection with the above-indicated facts, the authors have attempted to clarify compositions of the complex compounds and of ion formation in the KBr · $AlBr_3$–Nitrobenzene system, on the basis of specific gravity, viscosity and cryoscopic study, including data on electroconductivity, transference numbers and electrolysis data which are to be found in the literature [1,5].

EXPERIMENTAL

Initial Compounds and Methods of Measurement. Aluminum bromide was prepared according to the Gustavson method [14], from aluminum shavings and bromine, and was then distilled repeatedly and stored in sealed flasks. Potassium bromide was crystallized from aqueous solution, and then dried and stored in a dessicator. Nitrobenzene was prepared according to the Gatterman method [15] from benzene which was thoroughly purified beforehand, and the former purified by repeated washing with water, followed by soda solution, and then with water, dried over calcium chloride, distilled, and stored in sealed flasks.

All solutions were prepared in such manner that for all cases the ratio of aluminum bromide to nitrobenzene remained constant, with variation in amount of potassium bromide in the solution.

Since aluminum bromide hydrolysis can affect drastically the results of measurements, the authors directed their attention to the problem of protecting the solution from moisture during preparation and work with same, all measurements being carried out in containers and apparatus with hermetic seals.

Specific gravity was determined in standard manner by pycnometer in a thermostat at 20°. Viscosity measurements on the solution at 20° were carried out in an Ostwald viscometer of modified construction for the use of anhydrous solutions, permitting a satisfactory insulation of solution from air moisture during measurements. Cryoscopic measurements were carried out in standard form, using a Beckman apparatus with electro-magnetic stirrer. The solution under investigation was insulated in the Beckman apparatus from external air by means of a well-ground stopper and a ground connection through which the thermometer was introduced into the container.

Measurement Results and Their Evaluation

The insolubility of KBr in nitrobenzene, and its solubility, with heat evolution, in nitrobenzene solutions of $AlBr_3$, the increased electroconductivity of nitrobenzene solutions of $AlBr_3$ upon adding KBr [1-6], undoubtedly indicate complex formation in the system KBr · $AlBr_3$–Nitrobenzene.

Sheka and Pechenaya [5], upon studying the transference numbers of ions in the system indicated, came to the conclusion that $AlBr_4^-$ is the anion in this system, and that K^+ and $Al^{+++} \cdot nC_6H_5NO_2$ are the cations. Moreover, this makes possible the existence of complex cations in the solution which contain more than one potassium atom per ion.

On the basis of their results, however, [illegible] equally plausible conclusion can be reached concerning formation of a complex compound of the composition KAl_2Br_7, and its dissociation into the cations K^+ and $Al^{+++} \cdot nC_6H_5NO_2$, and the anion Al_2Br_7.

Specific Gravity and [illegible] of The KBr · $AlBr_3$—Nitrobenzene System.

Change in specific gravity and [illegible] of the system in relation to the molar ratio $\frac{KBr}{AlBr_3}$ in the solution were studied by the authors within the molar ratio [illegible] 1.13. Results [illegible] the specific gravity and viscosity measurements for the KBr · $AlBr_3$— nitrobenzene [illegible] are given in Table 1, and presented graphically in the form of curves $d = f_1\left(\frac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\frac{KBr}{AlBr_3}\right)$ (Figs. [illegible] 2).

As the data of Table 1 indicate, the specific grav[illegible] the viscosity of the system increase gradually with increase in the molar ratio of $KBr/AlBr_3$ in the solution, [illegible]ing from 0.134 to 0.509; they decrease in the range 0.509 to 0.712, and from 0.712 to 0.967 they again increase, reaching a maximum value, and then remaining constant with further increase in molar ratio of $\frac{KBr}{AlBr_2}$ in the solution.

TABLE 1
Specific gravity and viscosity for the system KBr · $AlBr_3$—Nitrobenzene
$C_6H_5NO_2$—14.400 g, $AlBr_3$—0.5000 g

Experiment number	KBr (in g)	$\frac{KBr}{AlBr_3}$ (in moles)	d	η (in centipoises)
1	-	-	1.2232	2.1173
2	0.0299	0.134	1.2242	2.1141
3	0.0553	0.247	1.2244	2.1268
4	0.0986	0.443	1.2270	2.1314
5	0.1132	0.509	1.2296	2.2546
6	0.1201	0.540	1.2288	2.2059
7	0.1420	0.638	1.2285	2.1345
8	0.1585	0.712	1.2276	2.0297
9	0.1753	0.788	1.2289	2.0464
10	0.1852	0.832	1.2311	2.0937
11	0.2007	0.902	1.2328	2.0965
12	0.2153	0.967	1.2345	2.4791
13	0.2505	1.126	1.2343*	2.4787*
14	0.2517	1.130	1.2345*	2.4791*

It should be mentioned that according to the authors' observation, for molar ratios of $\frac{KBr}{AlBr} > 0.967$, potassium bromide is almost insoluble in a nitrobenzene solution of aluminum bromide, i.e., it ceases to interact with aluminum bromide, and the solution becomes saturated with respect to potassium bromide.

It can be seen from Figs. 1 and 2 that two maxima and one minimum, individually, can be found on the $d = f_1\left(\frac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\frac{KBr}{AlBr_3}\right)$ curves.

Appearance of the first maximum of molar ratio $\frac{KBr}{AlBr_3} = 0.509$ is apparently connected with formation of a complex compound of the composition KAl_2Br_7 in the solution; the appearance of a second maximum of molar ratio $\frac{KBr}{AlBr_3} = 0.967$ corresponds to formation of a complex compound of the composition $KAlBr_4$ in the solution, which can be presented schematically by means of equations:

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* The solution was saturated with respect to KBr.

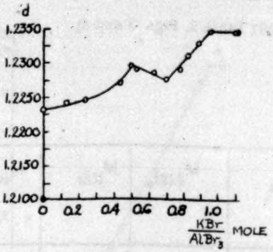

Fig. 1. Specific gravity of the KBr · $AlBr_3$—Nitrobenzene System.

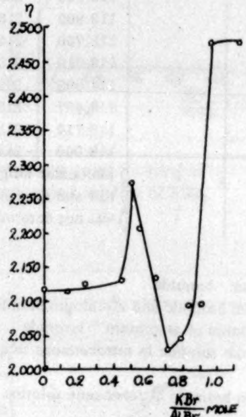

Fig. 2. Viscosity of the KBr · $AlBr_3$—Nitrobenzene System

$$KBr + (AlBr_3)_2 \rightleftharpoons KAl_2Br_7,^{*} \quad (1)$$

$$KAl_2Br_7 + KBr \rightleftharpoons 2KAlBr_4. \quad (2)$$

The presence of complex compounds of the compositions KAl_2Br_7 and $KAlBr_4$ in solution, for molar ratios $\frac{KBr}{AlBr_3}$ equal, respectively, to 0.509 and 0.967, are found to be in full accord with the authors' results from cryoscopic investigation, as well as with the results from electroconductivity measurements [1], and from transference numbers [5].

The appearance of a minimum on the $d = f_1\left(\frac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\frac{KBr}{AlBr_3}\right)$ curves for molar ratio $\frac{KBr}{AlBr_3} = 0.712$ is, in the authors' opinion, the result of a reaction occurring in the solution

$$KAl_2Br_7 + KBr \rightleftharpoons 2KAlBr_4,$$

because of which there occurs in solution a substitution of the KAl_2Br_7 molecule for a $KAlBr_4$ molecule.

It can be seen from the reaction equation that, on the one hand, new molecules appear, and on the other hand, upon addition of potassium bromide, two particles of another complex compound of the composition $KAlBr_4$ appear in the solution, instead of one particle of complex compound, having the composition KAl_2Br_7, which leads to a sharp change in concentration of particles in the solution. Two factors, in the main, affect specific gravity and viscosity between the first and second maxima: the 1st factor, which is conditioned by the nature of the newly-formed complex molecules, and the 2nd factor, which is conditioned by the change in concentration of particles in the solution.

The first factor decreases specific gravity and viscosity of the system; the second factor increases these properties. Before the minimum is reached, the first factor evidently dominates over the second; after the minimum is reached, the reverse phenomenon takes place, and minima appear as the result on the $d = f_1\left(\frac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\frac{KBr}{AlBr_3}\right)$ curves. The possibility of solvation of the particles by nitrobenzene during the process is not excluded, which will also be evident in a definitive manner upon changes in viscosity and specific gravity for the system.

Stability in specific gravity and viscosity of the system after the second maximum, for molar ratios of $\frac{KBr}{AlBr_3} > 0.967$ is apparently tied up with the fact that KBr no longer enters into reaction with the complex molecules, the solution becoming saturated with respect to it, and hence the concentration of the complex compound in the solution remains constant, which, naturally, will not be evident in change of specific gravity and viscosity of the solution.

In such a situation, the $d = f_1\left(\frac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\frac{KBr}{AlBr_3}\right)$ curves will proceed parallel to the abscissa axis, as was indeed observed by the authors.

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* Cryoscopic measurements have indicated that aluminum bromide is found in the form of dimer molecules in nitrobenzene.

Cryoscopy of the $KBr \cdot AlBr_3$–Nitrobenzene System.

For the purpose of a detailed clarification of the problem of complex formation and electrolytic dissociation of complex compounds, for the system $KBr \cdot AlBr_3$ –nitrobenzene, the authors carried out cryoscopic measurements of the solution with molar ratios $\frac{KBr}{AlBr_3}$ over the range of 0.166 to 1.130 (Table 2, Figs. 3 and 4).

TABLE 2

Cryoscopy of $KBr \cdot AlBr_3$–Nitrobenzene System

$C_6H_5NO_2$ – 14.400 g

Expt. no.	$AlBr_3$ (in g)	KBr (in g)	Molar ratio $\frac{KBr}{AlBr_3}$	t_0	t_1	t_2	Δt	Δt_1	Δt_2	M_{AlBr_3}	M_{KBr}	$M_{complex}$
1	–	–	–	5.503								
2	0.5000	–	–		4.782		0.721			331.811		
3	0.5000	0.0379	0.166			4.634		0.148	0.869		122.500	251.400
4	0.5000	0.0420	0.187			4.615		0.167	0.888		120.338	221.000
5	0.5000	0.1050	0.471			4.378		0.424	1.125		118.200	246.800
6	0.5000	0.1190	0.535			4.307		0.475	1.196		119.869	218.400
7	0.5000	0.1540	0.690			4.161		0.621	1.342		118.700	214.100
8	0.5000	0.1699	0.765			4.095		0.687	1.408		118.710	213.100
9	0.5000	0.1928	0.866			3.977		0.805	1.526		114.595	209.600
10	0.5000	0.2043	0.912			3.957		0.825	1.546		118.487	213.300
11	0.5000	0.2090	0.941			3.935		0.843	1.568		118.710	213.000
12	0.5000	0.2146	0.960			3.915		0.867	1.588		118.000	212.900
13	0.5000	0.2505	1 126			3.910		0.872	1.593		Molecular weight of KBr and the complex was not determined•	
14	0.5000	0.2517	1.130			3.916		0.866	1.587			

t_0 = freezing temperature of nitrobenzene

t_1 = freezing temperature of nitrobenzene solution of aluminum bromide

t_2 = freezing temperature of nitrobenzene solution of potassium bromide and aluminum bromide.

$t_0 - t_1 = \Delta t$ = lowering of freezing point of nitrobenzene solution of aluminum bromide

$t_1 - t_2 = \Delta t_1$ = lowering of freezing point of potassium bromide solution in nitrobenzene solution of aluminum bromide

$t_0 - t_2 = \Delta t_2$ = lowering of freezing temperature of potassium bromide nitrobenzene solution and aluminum-bromide nitrobenzene solution

M_{AlBr_3} = molecular weight of the aluminum bromide

M_{KBr} = molecular weight of the potassium bromide

$M_{complex}$ = molecular weight of the complex compound

Molecular weights were calculated according to a standard formula; cryoscopic constant for nitrobenzene was adopted as 6.89.

It can be seen from the data of Table 2 that the experimental M_{AlBr_3} = 331.811, while the theoretical was M_{AlBr_3} = 266.73. Thus, the experimental molecular weight of aluminum bromide was found to be higher than the theoretical weight corresponding to monomeric molecules, and lower than the theoretical corresponding to dimer molecules. Taking into account the relatively good electroconductivity of aluminum bromide nitrobenzene solution, indicative of electrolytic dissociation of aluminum bromide [6,7], the authors concluded that aluminum bromide in nitrobenzene is in the form of dimer molecules.

It can also be seen from the data of Table 2 that upon increasing the amount of potassium bromide in the solution, the freezing temperature of the aluminum bromide and the potassium bromide in nitrobenzene solution decreases,

• Solution was saturated with respect to KBr and the complex compound.

and the freezing point lowering increases.

The effect of potassium bromide upon freezing point lowering of aluminum bromide nitrobenzene solution is presented graphically in the form of curves $\Delta t_1 = f_3\left(\frac{KBr}{AlBr_3}\right)$ and $\Delta t_2 = f_4\left(\frac{KBr}{AlBr_3}\right)$ in Figs. 3 and 4.

The curves indicate that there exists a direct relationship between the freezing point lowering for the solution and the molar ratios of $\frac{KBr}{AlBr_3}$, which breaks down with molar ratios of $\frac{KBr}{AlBr_3} > 0.967$.

The rectilinear character of curves $\Delta t_1 = f_3\left(\frac{KBr}{AlBr_3}\right)$ and $\Delta t_2 = f_4\left(\frac{KBr}{AlBr_3}\right)$ is evidently related to the fact that potassium bromide combines with aluminum bromide in nitrobenzene; because of this fact, therefore, complex compounds are formed with a degree of electrolytic dissociation which is greater than the degree of dissociation of aluminum bromide dimer molecules, i.e., there occurs in the solution a replacement of molecules which are less dissociated by those of more dissociated complex molecules, and hence the concentration of particles in the solution increases, and thus the freezing point lowered as the result.

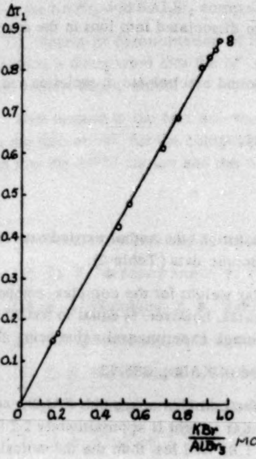

Fig. 3. Freezing point lowering of KBr solution in a nitrobenzene solution of $AlBr_3$.

The above-given hypothesis has been fully confirmed by the author's results according to investigations of specific gravity and electroconductivity of the system, $KBr \cdot AlBr_3$ – nitrobenzene, with respect to a molar ratio of $\frac{KBr}{AlBr_3}$ in the solution.

Plotnikov and Gorenbein [1] studied electroconductivity of the $KBr \cdot AlBr_3$ – nitrobenzene system in relation to a molar ratio of $\frac{KBr}{AlBr_3}$ within the molar ratio range of 0.103 to 0.861 where for the increased molar ratio of $\frac{KBr}{AlBr_3}$ in solution, electroconductivity increases all the time, and the $\kappa = f\left(\frac{KBr}{AlBr_3}\right)$ curve has a rectilinear character.

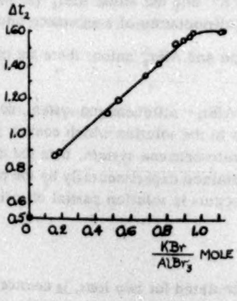

Fig. 4. Freezing point lowering of a nitrobenzene solution of KBr and $AlBr_3$.

On the basis of cryoscopic measurements, the author has calculated the molecular weight of potassium bromide at various molar ratios of $\frac{KBr}{AlBr_3}$ in the solution. It can be seen from the data of Table 2 that the experimental molecular weight of potassium bromide remains almost constant for all of the experimental cases, and almost equal to the theoretical. The theoretical molecular weight of KBr is equal to 119.012, and the experimental value for all investigated cases fluctuated within the range 114.595 to 122.5; the average experimental molecular weight for KBr was equal to 118.81.

Considering that the potassium bromide molecules combine with aluminum bromide molecules, and also the fact that upon electrolysis of the $KBr \cdot AlBr_3$ – nitrobenzene system cations, K^+, are discharged at the cathode, the author believes that the complex compounds formed by potassium and aluminum bromides are dissociated in solution, with almost 100% freeing of the K^+ cations. Such a hypothesis completely clarifies the equality between experimental and theoretical molecular weights for potassium bromide in the situation of its combination with aluminum bromide in solution.

Results of the author's measurements of specific gravity and viscosity for the $KBr \cdot AlBr_3-$ nitrobenzene system indicate that for a molar ratio of $\frac{KBr}{AlBr_3} = 0.509$ the complex compound KAl_2Br_7 exists in solution, and with $\frac{KBr}{AlBr_3} = 0.967$, and higher, $KAlBr_4$.

Cryoscopic measurements indicated that the complex compounds are dissociated into ions in the direction of K^+ ion formation, almost 100%.

Proceeding from the above-indicated, the process of complex compound electrolytic dissociation can be presented in the form of the following equations:

$$KAl_2Br_7 \rightleftharpoons K^+ + Al_2Br_7^-,$$

$$KAlBr_4 \rightleftharpoons K^+ + AlBr_4,$$

with the degree of dissociation close to unity.

In order to clarify the problem of the presence of other ions in the solution, the author carried out calculations of molecular weights for complex compounds on the basis of his own cryoscopic data (Table 2).

As can be seen from the data of Table 2, the experimental molecular weight for the complex compound KAl_2Br_7 fluctuates within the range of 221 - 251.4; the average experimental, however, is equal to 239.73; the complex compound $KAlBr_4$ fluctuates within the range 209.6 - 218.4, the average experimental value being 213.49.

The theoretical molecular weight of KAl_2Br_7 is equal to 652.448, and of $KAlBr_4$, 385.73.

If a comparison is made of the experimental molecular weights for the complex compounds KAl_2Br_7 and $KAlBr_4$ with the theoretical, for compound KAl_2Br_7 the experimental molecular weight is approximately 2.7 fold less than the theoretical, while for the compound $KAlBr_4$ it is approximately 1.85 fold less than the theoretical.

With regards to the above-indicated, the author has come to the conclusion that $KAlBr_4$ is dissociated into two ions, the K^+ cation and the $AlBr_4^-$ anion, with the extent of dissociation close to unity.

With respect to the complex compound KAl_2Br_7, the latter is apparently dissociated on the whole into the cation K^+ and the anion $Al_2Br_7^-$, but the existence of other ions in the solution must be admitted, since, during dissociation of the two ions, the experimental molecular weight, as compared with the theoretical (even with 100% dissociation) would be 2-dolf less, when according to the author's data, it was found to be 2.7-fold less.

The fact that other ions exist in the solution besides the K^+ cation and the $Al_2Br_7^-$ anion, is confirmed by results obtained by Sheka and Pechenaya, from a study of the transference numbers for the $KBr \cdot AlBr_3-$ nitrobenzene system. According to their results, the sum of the transference numbers for the cation K^+ and the anion $AlBr_4^-$ (or the equivalent $Al_2Br_7^-$ anion), is considerably less than unity, which cannot occur during dissociation of a substance into two ions.

Sheka and Pechenaya consider that in solution, apart from the K^+ cation and $AlBr_4^-$ anion, there are complex cations present which contain more than one potassium atom per ion.

The author's results, according to cryoscopic investigation of the $KBr \cdot AlBr_3-$ nitrobenzene system, do not confirm the deductions of Sheka and Pechenayay concerning the presence of ions in the solution which contain more than two potassium atoms per ion. If such ions truly did exist in the $KBr \cdot AlBr_3-$ nitrobenzene system, then the molecular weight of potassium bromide could not be equal to the theoretical, as was obtained experimentally by the present author. More probable, in the author's opinion, is the hypothesis that there occurs in solution partial dissociation of the complex $Al_2Br_7^-$ anion into more simple ions, according to the equation

$$Al_2Br_7^- \rightleftharpoons Al^{+++} + AlBr_7^{----},$$

resulting from which is the fact that the sum of the transference numbers, calculated for two ions, is considerably less than unity, and the experimental molecular weight for the compound, KAl_2Br_7 is 2.7-fold less than the theoretical.

SUMMARY

1. Aluminum bromide in nitrobenzene is found to be in the form of dimeric molecules, $(AlBr_3)_2$, partially dissociated into ions.

2. A study of cryoscopy, specific gravity and viscosity indicates the fact that potassium bromide forms two complex compounds with aluminum bromide: with a molar ratio $\frac{KBr}{AlBr_3} = 0.509$, compound of the composition KAl_2Br_7;

and with a molar ratio $\frac{KBr}{AlBr_3}$ = 0.967, compound of the composition $KAlBr_4$.

3. Equality of the experimental molecular weight with the theoretical for potassium bromide, and also the fact that during the electrolytic process, potassium cation is discharged on the cathode, indicate almost complete dissociation of the $KAlBr_4$ and KAl_2Br_7 compound into ions in the direction of K^+ cation formation.

4. Results of determination of the molecular weight of complex compounds signify that the compound $KAlBr_4$ in solution is dissociated into the K^+ cation and the $AlBr_4^-$ anion, the compound KAl_2Br_7 being dissociated into the K^+ cation and the $Al_2Br_7^-$ anion.

With respect to the fact that the sum of the transference numbers calculated for two ions is considerably less than the theoretical for the compound KAl_2Br_7, it must be admitted that there is partial dissociation of the $Al_2Br_7^-$ anion into the Al^{+++} cation and the $AlBr_7^{----}$ anion.

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HEAT OF DILUTION OF DIOXAN AND WATER

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The dioxan – water system has been studied for surface tension, density, vapor pressure, refractive index and freezing point [1]. None of the property-composition diagrams, except that for density, offer information about formation of compounds of the components in this system. However, the density isotherm shows a clearly defined maximum at 32 mole % of dioxan, which may be related to the formation of a hydrate type compound.

Taking the foregoing as a starting point, we undertook to study the heat of dilution of the dioxan – water system.

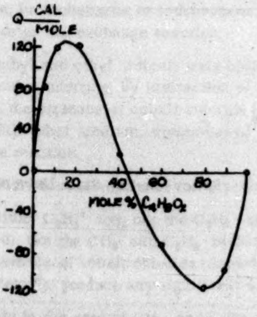
The heat of dilution was measured in a calorimeter with isothermic shield, as described previously [2].

The components, weighed out in calculated quantities, were placed in two communicating glass vessels in the calorimetric liquid. They were mixed at the appropriate moment, being transferred from vessel to vessel by air pressure. The temperature in the calorimeter was measured to an accuracy of 0.001° by an ordinary metastatic thermometer. Correction for heat exchange was computed by the Regnaud-Pfaundler-Usov equation. The heat value of the calorimeter system was determined after each experiment by dissolving potassium chloride in the calorimeter water.

Purification of the components of the system under study was performed as follows.

After extraction over anhydrous calcium chloride, the dioxan was distilled. The distillate, which condensed in the 99.6-100.5° interval, was glaciated at 4-7°. The crystals were liberated from the liquid phase by means of a Buchner funnel and transferred to a flask with metallic sodium. After three days the dioxan was distilled (in the 100.1-100.8° interval). The pure dioxan froze completely at 12.2°, which is close to the figure given in the literature [1].

The table presents the results of determination of the heat of dilution of the dioxan-water system.* The figure represents a diagram plotted on the numerical data in the table.



Variation of heat of dilution of dioxan and water with content of dioxan.

Heat of Dilution of Dioxan and Water

Dioxan (mole %)	Heat of dilution, in calories per one mole of mixture
0.0	0.0
5.0	80.6
10.0	118.1
20.0	121.4
40.0	16.5
60.0	−69.6
70.0	− 99.6
80.0	− 112.0
90.0	−94.8
100.0	0.0

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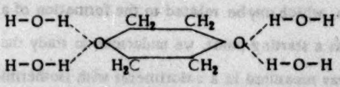
[*] The heats of dilution of this system were studied at the suggestion of N. A. Trifonov and M. Z. Tsinin.

It is clear from the figure that the curve of heats of dilution for this system is S-shaped, and that the portion of the curve corresponding to high concentrations of dioxan lies below the axis of the mixture.

According to the usual system of classification, this type of curve reflects the occurrence of two simultaneous processes, to wit, the decomposition of associated molecules, accompanied by a negative thermal effect, and the formation of a compound, partially dissociated in the liquid phase, accompanied by a positive effect. Similar isotherms for heat of dilution have been obtained by E. and M. Bose [3], for system consisting of water and ethyl or propyl alcohols.

As the dimolar moment of the dioxan molecule is about 0.4 D, and that of water is 1.84 D, it must be assumed that the negative portion of the curve corresponds to the decomposition of the associated water molecules upon dilution. The positive portion of the curve is related in all probability to the interaction of the components, with the formation of a complex of low thermal stability. This reaction between dioxan and water apparently amounts to the formation of intermolecular hydrogen bonds of the type



The fact that dioxan readily gives oxonium compounds, and reacts with bromine, iodine and sulfuric acid to form solid crystalline substances is well known. Favorsky describes their structure by means of a formula in which oxygen is tetravalent [4].

SUMMARY

In a dioxan-water system the isotherm of heat of dilution has positive and negative segments, which may be explained by the formation of a molecular compound of water and dioxan of the hydrate type, and the decomposition of an associated component −water.

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EXCHANGE OF BOUND RADICALS BY FREE RADICALS AND IONS IN SOLUTION

I. P. Gragerov

The behavior of free radicals in solution has been inadequately studied. In particular, very little is known concerning the possibility of their exchange reactions of the type:

$$R_1\cdot + :X-R \rightarrow R_1-X: + R\cdot. \qquad (1)$$

It might be expected that such reactions would not proceed with too great a difficulty since, by analogy with hydrogen isotope exchange, it could be accomplished by the approach of $R_1^{\cdot}$ toward the free electron pair, with simultaneous withdrawal of $R\cdot$, which, apparently, requires only a small activation energy. Exchange reaction for positive ions whose formation as intermediate products is frequently postulated , should, one would think, proceed in analogous fashion, but with greater ease.

Existence of a reaction of the type mentioned was proposed by Kharasch and coworkers [1] for the case of interaction of free methyl with diethyl ether, and by Nesmeyanov and Makarova [2], Kursanov and Setkina [3], for some reactions where positive ions participate.

A study of the exchange reaction of free radicals of positive organic ions is of great interest for the understanding of chemical process mechanisms. Such data have an added significance, where, for $R_1 = R$ exchange is initiated by chains, which ensures an increase in concentration of radical $R\cdot$, which can play an important role in directing the radical reaction in the required direction.

In the present work the possibility of, and conditions for, an exchange reaction of type (1), for $R_1 = R$, with deuterium labelled free phenyl, ethyl and methyl radicals, and the positive phenyl ion, have been studied. The isotope method not only makes it possible to study exchange between identical radicals, but also the exchange mechanism in the purest form, and makes possible ready separation of the reaction products.

As the source of phenyl radicals, the thermal decomposition reaction of heavy phenyldiazonium chloride [2], or the photodecomposition of heavy iodobenzene, was used. The source of $C_6D_5^+$ was the decomposition reaction of heavy phenyldiazonium borofluoride [2]. The indicated conversions were carried out in light diphenyl ether, phenetole, bromobenzene or iodobenzene, whose molecules, having free electron pairs, can, according to our postulates, undergo the exchange reaction.

Methyl and ethyl radicals were obtained by photochemical decomposition of heavy methyl iodide or heavy ethyl iodide, and in addition, by interaction of phenylmagnesium bromide with heavy methyl iodide, or heavy ethyl bromide, in the presence of cobalt chloride [1]. These transformations were carried out in anisole, phenetole, diethyl or methylbutyl ether medium, molecules of which contain the methyl or ethyl radicals at an oxygen, and can undergo exchange reaction.

Conditions and results of the experiments carried out are given in the Table.

Neither $C_6H_5^+$ ion, nor the $C_6H_5\cdot$ radical, which form upon thermal decomposition of diazonium salts (Experiments 1-6), nor the $CH_3\cdot$ and $C_2H_5\cdot$ radicals, generated by interaction of phenylmagnesium bromide with alkyl halides in the presence of cobalt chloride (Experiments 10 and 11), nor the $C_6H_5\cdot$ radical formed by photolysis of iodobenzene (Experiment 7), produce any significant exchange with corresponding radicals bound to oxygen, bromine or iodine.

Only in the case of $CH_3\cdot$ and $C_2H_5\cdot$ radicals of photochemical origin (Experiments 8 and 9) was the exchange found to exceed experimental error considerably, and determined with certainty.

The fact was that in a number of cases (Experiments 1,2,3,5,6), and particularly 8 and 9), despite the absence of any significant exchange, part of the deuterium of the initial heavy component was lost; this can be explained (in the case of Experiment 8) by a side reaction of the following type:

$$C_6H_5OCH_3 + I\cdot \rightarrow C_6H_5O\cdot + CH_3I,$$

in which the forming light methyl iodide dilutes the initial heavy material.

TABLE
Conditions and Results of the Exchange Experiments

Experiment No.	Substances exchanged	Experimental conditions (temp. or time of illumination)	Excess water density from burning, in γ units				Percent exchange*
			Initial heavy compound	Calculated for radicals being exchanged, both compounds in equilibrium	Found in the heavy component	Found in the exchanging radical of the light component	
1	$C_6D_5^+$ from 6 g $C_6D_5N_2BF_4$ and 18.3 g C_6H_5Br	about 85°; sec.	1596	339	1412	−2	–
2	$C_6D_5^+$ from 6 g $C_6D_5N_2BF_4$ and 21.4 g C_6H_5I	"	1596	331	1388	10	–
3	$C_6D_5^+$ from 5.6 g $C_6D_5N_2BF_4$ and 12.5 g $(C_6H_5)_2O$	"	1596	263	1488	14	–
4	$C_6D_5\cdot$ from 8.5 g $C_6D_5N_2Cl$ and 22.7 g C_6H_5Br	about 100°; sec	1596	471	1575	40	–
5	$C_6D_5\cdot$ from 4.5 g $C_6D_5N_2Cl$ and 17.6 g C_6H_5I	"	1596	478	1482	35	–
6	$C_6D_5\cdot$ from 4.6 g $C_6D_5N_2Cl$ and 12.7 g $(C_6H_5)_2O$	"	1596	302	1482	13	–
7	7.8 g C_6D_5I and 3.9 g $C_6H_5OCH_3$	Exposure 100 hours	1480	760	1459	24	–
8	6.2 g C_2D_5I and 4.7 g $C_6H_5OC_2H_5$	Exposure 104 hours	1118	569	771	134	24
9	4.8 g CD_3I and 6.0 g $C_6H_5OCH_3$	Exposure 200 hrs.	1593	600	1206	77	13
10	$CD_3\cdot$ and $C_4H_9OCH_3$	70°; sec.	723	ca 112**	571***	28	–
11	$C_2D_5\cdot$ and $C_2H_5OC_2H_5$	34°; sec.	1817	ca. 115**	1735***	3	–

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* Calculated according to the deuterium content of light component in the exchange reaction.

** Approximate calculation, assuming uniform distribution of deuterium between the exchanging ether radical and methane, or ethane + ethylene.

*** In the resulting gas.

The data quoted indicate that the exchange reaction for the radicals studied proceeds with difficulty, and is observed only in rare instances.

The interesting fact of difference in behavior of the methyl and ethyl radicals of photochemical origin and the same radicals which form upon reaction of alkyl halides on phenylmagnesium bromide (Experiments 8,9 and 10,11) should be mentioned.

In conclusion we shall point to the fact that results from Experiments 10,11 and 5 do not agree with the data of Kharasch [1], who has indicated a change between the $CH_3 \cdot$ radicals and diethyl ether, nor with the data of Shaw [5], who found that iodobenzene reacts with $C_6H_5 \cdot$ radicals, producing the compound $C_6H_5-I-C_6H_5$, which should lead to an exchange. Apparently the conclusions reached by the above-mentioned authors, based upon circumstantial evidence, are erroneous.

EXPERIMENTAL

The synthesis of heavy iodobenzene, ethyl bromide, ethyl iodide and methyl iodide have been described in the preceding work [10.

Heavy diazonium salts were prepared from aniline, deuterium labeled in the m-position [6]. The aniline hydrochloride required for synthesis of anhydrous phenyldiazonium chloride [7] was prepared by drying a mixture of the equivalent amounts of heavy aniline and concentrated hydrochloric acid in a vacuum desiccator over alkali. The diazonium salt was prepared directly before use. Phenyldiazonium borofluoride was prepared according to the method described by Nesmeyanov, Kocheshkov and Nady [8].

Thermal Decomposition of Heavy Diazonium Salts in Bromobenzene, Iodobenzene, or Diphenyl Ether Medium

Phenyldiazonium chloride or borofluoride was placed in a three-necked flask equipped with stirrer and mercury seal, thermometer extending to the bottom, and a weighed amount of solvent added, and the reaction mixture heated on a water bath with stirring. Decomposition for the phenyldiazonium chloride began at 85-90°, and for phenyldiazonium borofluoride at 70-75°, degradation being carried out, respectively, at 95-100 and 80-90°, and terminated after 5-30 minutes. Reaction mass was then washed with potash solution, water, dried with $CaCl_2$, and distilled in vacuo, the fluorobenzene being collected in a trap cooled with liquid air. After several fractionations, pure chlorobenzene, or fluorobenzene, and solvent were obtained in a yield of 40-60 %. Purity of the resulting compounds was ascertained by specific gravity determination, which indicated that impurities did not exceed 0.5-2%.

The exchange reaction for $C_6H_5 \cdot$ radicals, or for $C_6H_5^+$ ions, produced by decomposition of the diazonium salts, leads to the conclusion that the atomic chlorine or fluorine ions which are forming simultaneously, do not combine with either the heavy radical or the ion, but rather with the light, displaced, according to reaction type (1), from the solvent. In this case, the deuterium content of chlorobenzene or of fluorobenzene becomes less than in the initial diazonium salts. On the other hand, a corresponding amount of deuterium gets into the solvent. Therefore, to answer the question of presence or absence of exchange, the chlorobenzene, diphenyl ether, bromobenzene, or iodobenzene, isolated from the reaction mixture, was burned and the water analyzed for deuterium content. Burning of fluorobenzene was found to be inconvenient since the hydrogen fluoride formed reacted with glass and quartz. Fluorobenzene, therefore, was converted to diphenyl,* it being possible to analyze for deuterium content in the latter case without any difficulty.

Photochemical Decomposition of Heavy Iodobenzene, Methyl Iodide and Ethyl Iodide in Anisole or Phenotole Medium**

A mixture of methyl iodide or iodobenzene with anisole, or a mixture of ethyl iodide with phenetole, was placed in a quartz flask and illuminated with a quartz lamp PRK-2, (cooling by running water). After cessation of exposure, the reaction mixture was washed with potash, dried, and the initial iodide and solvent isolated by fractionation in vacuo, adequate purity of which was confirmed by specific gravity determination. In all experiments of this series, there was obtained upon distillation a considerable amount of high-boiling substances, appearing upon conversion of the radicals and atomic iodine.

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* To convert fluorobenzene into diphenyl, the fluorobenzene was heated with metallic sodium at 100° for several hours [9]. The reaction product was extracted with ether. The residue, after removal from ether, was recrystallized from alcohol, or was sublimed in vacuo. Yield of biphenyl was small. Its m.p. was 67-70°.

** M. P Yakovleva participated in these experiments.

Compositions of the reaction products was investigated in greater detail in Experiment 8: before opening the sealed flask, its contents were cooled with liquid air, and the mixture of gases evolved upon reheating was collected in a gasometer, in the amount of 265 ml. Gases from the gasometer were passed through a bromine trap, and a substance with b.p. about 131° and d_4^{20} 1.5374 was formed, corresponding to the constants for ethylene bromide, and proving the presence of ethylene in the mixture investigated. The second component (whose volume was found to be about 135 ml.) was apparently ethane. Ethyl iodide was distilled out from the liquid in the flask (in vacuo), and the residue was cooled to −30°. A substance precipitated out, which, after recrystallization from heptane, had a m.p. of 81.3-81.7°, corresponding to the literature data for symmetrical diiodoethane. Analysis of the iodine content confirmed the formation of diiodoethane:

Found %: I 90.18, 90.70. $C_2H_4I_2$. Calculated %: I 90.05.

In this experiment diiodoethane interferes with the isolation of pure phenetole. For decomposition of the diiodoethane, the phenetole fraction was heated with zinc dust before final purification.

We analyzed for deuterium content the water from combustion of iodobenzene and methyl and ethyl iodides, which if reaction (1) proceeds, should contain less deuterium than the initial iodide and the water from combustion of anisole and phenetole, which, according to reaction (1) should have higher deuterium content.

Possibility of Ethyl and Methyl Radical Exchange with Diethyl and Methylbutyl Ethers

Free radicals in these experiments were generated according to the reaction

$$2C_6H_5MgBr + 2C_2D_5Br(\text{or } 2CD_3I) \rightarrow C_6H_5-C_6H_5 + 2MgBr_2(\text{or } 2MgBrI) + 2C_2D_5\cdot(\text{or } 2CD_3\cdot).$$

1.27 g of anhydrous cobalt chloride, 10.9 g of heavy ethyl bromide and 7.5 g of anhydrous diethyl ether (or 0.44 g $CoCl_2$, 5 g of CD_3I and 4.4 g of $C_4H_9OCH_3$) were placed in a three-necked flask. To this mixture was added, dropwise, with stirring, 22.8 g of phenylmagnesium bromide solution in 32.5 g of anhydrous ether (or a solution of 8.5 g of C_6H_5MgBr in 12.5 g of $C_4H_9OCH_3$). Upon pouring the mixture boiled. The evolving gases were passed through a trap cooled to −80°, and were collected in a gasometer. Their volume amounted to 1.85 half-ounces (or 0.55 liters), which corresponded to about 70% yield of theoretical.

The reaction mixture was treated with water, and then all of the liquid from the flask distilled in vacuo by heating on a water bath. The ether layer was separated and was boiled for many hours over metallic sodium and distilled to remove alkyl halide. Test for adequate purity was made by determination of specific gravity.

Ether and the gas mixture were burned and the resulting water analyzed for deuterium content.

In the case of exchange reaction by course (1), water of combustion of the ethers should have increased density. The gaseous products from the experiment with ethyl bromide (Experiment 11) consisted of ethane and ethylene, the amount of deuterium in which, for reaction course (1), should be lower than for initial ethyl bromide. In the experiment with methyl iodide (Experiment 10), the gas consisted principally of methane, formed by rupture of hydrogen from the methyl radicals of the reaction mixture. In a majority of cases the molecule which did not have deuterium gave up hydrogen. Therefore, in the absence of reaction course (1), methane combustion should produce water with a deuterium content approximately 25% lower than for the initial methyl iodide, i.e., water with an excess density of about 543 γ. In the case of exchange reaction (1), the density of water should be lower.

Water resulting from combustion of the compounds isolated from the experiments after addition of a small amount of alkali, was analyzed for deuterium content by the microflotation method, with an accuracy of ± 3%.

SUMMARY

1. Exchange between free phenyl, methyl and ethyl radicals labeled with deuterium and positive phenyl ions, obtained by various means, has been studied, as well as the same radicals which compose the compounds.

2. It has been established that exchange reactions are observed only for free methyl and ethyl of photochemical origin, and do not proceed with the same radicals obtained by other means.

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INTERACTION OF 8-HYDROXYQUINOLINE WITH ORGANIC ACID ANHYDRIDES, STUDIED BY THE METHOD OF PHYSICO-CHEMICAL ANALYSIS

D. E. Dionisyev and Z. K. Dzhelomanova

8-Oxyquinoline, as an amphoteric compound, behaves as a base in its reactions with mineral acids and forms addition compounds with them, in which one equivalent of acid combines with one molecule of 8-oxyquinoline [1]. We have shown previously [2] that 8-oxyquinoline reacts with acetic and salicylic acids to form compounds with a component ratio of 1 : 2 (2 molecules of acid), while with monochloracetic and benzoic acids it produces compounds of equimolecular composition, with p-nitrobenzoic acid it produces compounds that melt and dissociate, and with p-oxybenzoic, cinnamic and hydrocinnamic acids it does not form molecular compounds.

It is of interest to clarify how 8-oxyquinoline reacts with anhydrides of organic acids. That was our purpose in studying systems of 8-oxyquinoline and acetic, benzoic and phthalyl anhydrides in terms of fusibility, viscosity and electrical conductivity. We were the first to investigate the given systems. The methodology was the same as that we employed in our earlier studies [3]. Viscosity was expressed in centipoises and concentrations in molecular percentages.

The "pure" grade 8-oxyquinoline employed in this work was several times recrystallized from ethyl alcohol, and had a melting point of 75°, d_4^{80} 1.1594. The acetic anhydride was twice distilled with a fractionating column, and the fraction produced had a boiling point of 138-139°, d_4^{20} 1.082, and a melting point of −72°.

The benzoic anhydride was synthesized from benzoic acid by the action of acetic anhydride in the presence of phosphoric acid as a catalyst. It was purified by solution in benzene and recrystallized in petroleum ether. The melting point of the purified product was 42°, the boiling point 360°, and d_4^{95} 1.139.

The phthalyl anhydride was purified by sublimation and had a melting point of 128° and a boiling point of 284.5°.

8-Oxyquinoline — acetic anhydride system. Results of fusibility studies of this system are shown in Fig. 1 (curve a), of viscosity studies in Fig. 2, and of electrical conductivity studies — in Fig. 3. The fusibility curve has one eutectic point and one maximum. The eutectic point, at a melting point of 41.5° corresponds to 65 mole % of 8-oxyquinoline. The maximum, at a melting point of 55.7°, is reached at 50 mole % of 8-oxyquinoline. It indicates the formation, in the solid phase, of a compound having the following composition $C_9H_7NO \cdot (CH_3CO)_2O$.

Viscosity, η, and electrical conductivity, κ, were measured at 75 and 85°.

Fig. 2. shows the viscosity isotherms to have a convex maximum, corresponding to 55 mole % of 8-oxyquinoline, shifted somewhat to the side of the more viscous component.

The electrical conductivity isotherms show a minimum, corresponding to 50 mole % of 8-oxyquinoline, and two maxima. When electrical conductivity is corrected for viscosity the $\kappa\eta$ minimum does not disappear. The viscosity and electrical conductivity data point to the formation of a compound of 1 : 1 ratio in the liquid phase.

8-Oxyquinoline — benzoic anhydride system. Findings are represented as follows: fusibility in Fig. 1, curve b; viscosity in Fig. 2, and electrical conductivity in Fig. 4.

The results shown in Fig. 1 make it clear that 8-oxyquinoline and benzoic anhydride combine into a compound with a melting point of 103° and a composition of 50 mole % 8-oxyquinoline and 50 mole % benzoic anhydride, the component ratio being 1 : 1. The first eutectic point, with a melting point of 49.5° corresponds to 75 mole % 8-oxyquinoline and the second, with a melting point of 32°, to 9 mole % of oxyquinoline.

Viscosity and electrical conductivity were measured at temperatures of 95 and 105°. The viscosity curves have a single point of inflexion at 50 mole % of 8-oxyquinoline and 50 mole % of benzoic anhydride. The viscosity of the benzoic anhydride – the more viscous component, is 2.497 centipoises at 95° and 2.097 centipoises at 105°, while the maximum viscosity of the system at 95° is 13.08 centipoises, and at 105°, 8.51 centipoises.

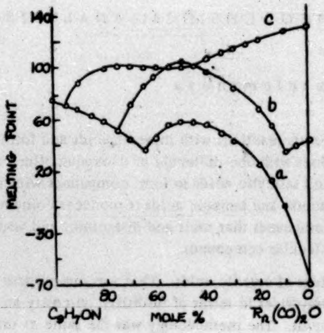

Fig. 1. Explanation in the text.

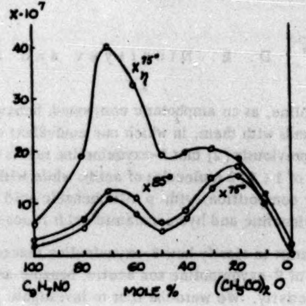

Fig. 3. Explanation in the text.

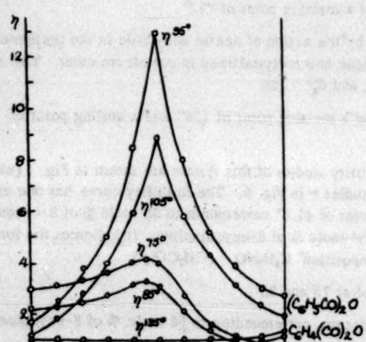

Fig. 2. Explanation in the text

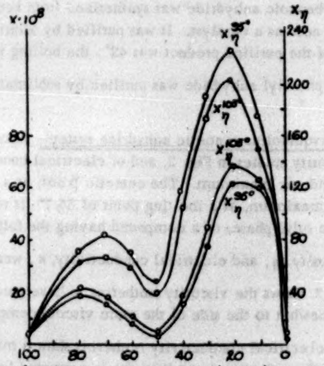

Fig. 4. Explanation in the text.

The electrical conductivity isotherms show a minimum corresponding to 50 mole % of 8-oxyquinoline. When electrical conductivity is corrected for viscosity the minimum neither disappears nor shifts. The liquid phase, too, shows a stable compound of 1 : 1 composition.

8-Oxyquinoline – phthalyl anhydride system. When the fusibility of this system is determined in the usual way, the result is a curve with a eutectic point indicating the absence of a chemical reaction between the components. However, after long heating the fusibility curve (Fig. 1) shows two eutectic points. The first eutectic point, with melting point of 71°, corresponds to 95 mole % of 8-oxyquinoline, and the second, with a melting point of

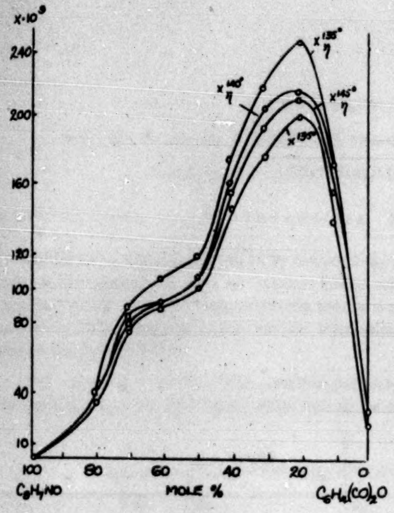

Fig. 5. Explanation in text.

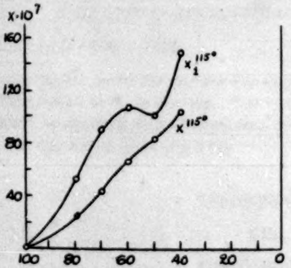

Fig. 6. Explanation in text.

99°, corresponds to 45 mole % of 8-oxyquinoline, indicating the formation of compounds undergoing rapid dissociation.

The viscosity study findings are presented in Fig. 2, and those for electrical conductivity in Figs. 5 and 6. At 135 and 145°, the viscosity curves are somewhat concave in the direction of the composition axis, and give no indication of the occurence of a reaction between the components.

The electrical conductivity curve, κ, determined at 115° (Fig. 6) takes the form of a hyperbola concave toward the composition axis. As temperature rises, the conductivity curves, measured at 135 and 145° (Fig. 5) show points of inflexion corresponding to 50 mole % 8-oxyquinoline. When conductivity is corrected for viscosity the points of inflexion do not disappear.

Conductivity curve κ_1 (Fig. 6) was measured after long-continued heating at 115°. It shows a minimum corresponding to 50 mole % 8-oxyquinoline. Thus, long-continued heating at 115° and heating to 135 and 145° showed reactions between the components in the liquid phase, resulting in a compound of the following formula $C_9H_7NO \cdot C_8H_4O_3$ with a 1 : 1 ratio between its components.

SUMMARY

1. The fusibility, viscosity and electrical conductivity methods were used to study the systems resulting from the reaction of 8-oxyquinoline with acetic, benzoic and phthalyl anhydrides.

2. The curves of viscosity, fusibility and electrical conductivity point to the formation of compounds of the following composition in the solid and liquid phases:

$C_9H_7NO \cdot (CH_3CO)_2O$, $C_9H_7NO \cdot (C_6H_5CO)_2O$ and $C_9H_7NO \cdot$

$\cdot\ C_6H_4(CO)_2O$.

The presence of two phenyl radicals in the anhydride formula facilitates reaction with 8-oxyquinoline, and the viscosity curve of the 8-oxyquinoline – benzoic anhydride system shows a single maximum.

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* T.p. = C.B. Translation pagination.

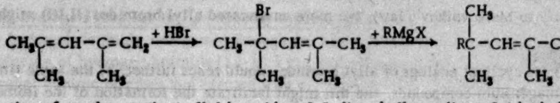
SYNTHESIS OF HYDROCARBONS

XLV. SYNTHESIS OF CYCLOHEXENE AND CYCLOHEXAND HYDROCARBONS WITH A QUATERNARY CARBON ATOM, BASED UPON 1,3-DIMETHYL CYCLOHEXADIENE-1,3

R. Ya. Levina, N. P. Shusherina, Kim Dyai Gir and E. G. Treshchova

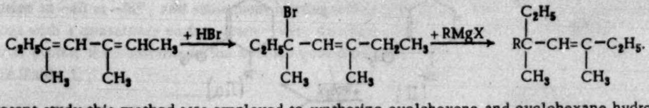
Our previous communications [1,2] described the reaction we developed as a method of synthesizing ethylene and paraffin hydrocarbons with a quaternary carbon atom. The method embraces two stages: the conversion of a diene hydrocarbon with a conjugate double bond to a tertiary hydrobromide of allyl type with a structure rendering an allyl rearrangement impossible, and the substitution of an organomagnesium compound radical for a free bromine atom in the hydrobromide.

The use in this reaction of 2,4-dimethylpentadiene hydrobromide, a tertiary allyl bromide, resulted in the production of 2,4,4-trimethylalkenes, while hydrogenation of the latter gave 2,4,4-trimethylalkanes [1].



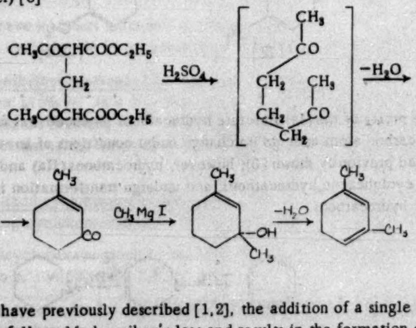
$$\underset{CH_3}{CH_3C}=CH-\underset{CH_3}{C}=CH_2 \xrightarrow{+HBr} CH_3-\overset{Br}{\underset{CH_3}{C}}-CH=\underset{CH_3}{C}-CH_3 \xrightarrow{+RMgX} R\overset{CH_3}{\underset{CH_3}{C}}-CH=\underset{CH_3}{C}-CH_3.$$

The reaction of another tertiary allyl bromide – 3,5-dimethylheptadiene-2,4 hydrobromide – with organomagnesium compounds was revealed to be a method of synthesizing a second group of hydrocarbons with a quaternary carbon atom – the 3,5-dimethyl-5-ethylalkenes, while their hydrogenation produced 3,5-dimethyl-5-ethylalkanes [2]

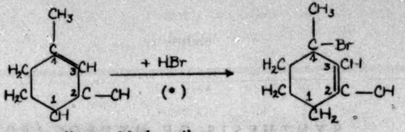


$$C_2H_5\underset{CH_3}{C}=CH-\underset{CH_3}{C}=CHCH_3 \xrightarrow{+HBr} C_2H_5\overset{Br}{\underset{CH_3}{C}}-CH=\underset{CH_3}{C}-CH_2CH_3 \xrightarrow{+RMgX} R\overset{C_2H_5}{\underset{CH_3}{C}}-CH=\underset{CH_3}{C}-C_2H_5.$$

In the present study this method was employed to synthesize cyclohexene and cyclohexane hydrocarbons with a quaternary carbon atom in the ring. The initial diene hydrocarbon was 1,3-dimethylcyclohexadiene-1,3, which was synthesized by reacting methylmagnesium iodide with 1-methyldyclohexen-1-one-3 (ketone cleavage product of methylene-bis-acetoacetic ether) [3]

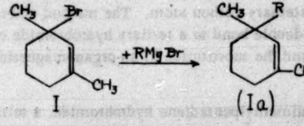


As with the alkadienes we have previously described [1,2], the addition of a single hydrogen bromide molecule to 1,3-dimethylcyclohexadiene follows Markovnikov's law and results in the formation of a tertiary allyl bromide (I), with structure rendering impossible the formation of an isomeric bromide by allyl rearrangement



(•) in 1,2 or 1,4 position, according to Markovnikov.

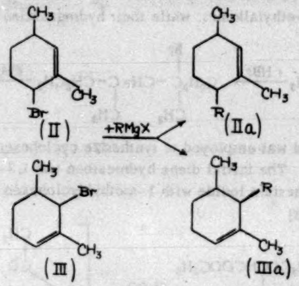
By reacting alkylmagnesium halogenides with that tertiary bromide having a free bromine atom, a number of cyclohexene hydrocarbons with a quaternary atom (Ia) were synthesized: 1,1,3-trimethylcyclohexene-2, 1,3-dimethyl-1-ethylcyclohexene-2 and 1,3-dimethyl-1-propylcyclohexene-2



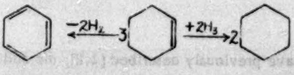
(where $R = CH_3, C_2H_5, C_3H_7$)

If the addition of hydrogen bromide to dimethylcyclohexadiene also followed the other possible directions (in accordance with and contrary to Markovnikov's law), two more unsaturated allyl bromides (II,III) might be formed in addition to bromide (I).

Bromides (II) and (III), as cyclical analogs of allyl bromide, would react further, at the same time as hydrobromide (I), with the organomagensium compounds, and this might facilitate the formation of the isomeric hydrocarbons (IIa) and (IIIa) as impurities in the main reaction products, the hydrocarbons with a quaternary carbon atom (Ia)



The question as to the purity of the (Ia) sturcture hydrocarbons produced was resolved thus: cyclohexene hydrocarbons with a quaternary carbon atom undergo no change under conditions of irreversible catalysis (Zelinsky's reaction [4]), as one of us had previously shown [5]; however, hydrocarbons (IIa) and (IIIa) should weakly resist this reaction, characteristic of cyclohexene hydrocarbons, and undergo transformation into a mixture of the corresponding cyclohexane and aromatic hydrocarbons



The presence of an aromatic hydrocarbon in the product of catalysis may readily be determined by the Raman spectra.

One of the hydrocarbons we synthesized – 1,3-dimethyl-1-ethylcyclohexene-2 ($R = C_2H_5$) was passed over platinized charcoal, at 200°, in a weak nitrogen current; the hydrocarbon was recovered unchanged, with the same constants as before catalysis, and readily discolored bromine water; study of the Raman spectra showed complete absence of any admixture of aromatic hydrocarbons.

It was thus established that the cyclohexene hydrocarbons we had produced possessed a quaternary carbon atom in the ring, that this was the reason for their passivity in the given catalytic reaction, and that they contained no admixture of their isomeric hydrocarbons.

Catalytic hydrogenation of the synthesized cyclohexenes resulted in the production of the corresponding cyclohexanes –1,1,3-trimethyl-1,3-dimethyl-1-ethyl- and 1,3-dimethyl-1-propylcyclohexanes. All the lines of maximum and medium intensity in the Raman spectrum of the first of these – 1,1,3-trimethylcyclohexane – corresponded to the lines described in the literature on that hydrocarbon [6,7].

EXPERIMENTAL

1-Methylcyclohexen-1-one-3 (b.p. 198-200° at 750 mm) was prepared with a 60% yield by Knoevenagel's method [3] – reacting dilute sulfuric acid with methylene-bis-acetoacetic ether.

1,3-Dimethylcyclohexadiene-1,3 was synthesized by reacting 1-methyl-cyclohexen-1-one-3 with methylmagnesium iodide as described by us previously to produce 2,4-dimethylpentadiene-1,5 [1]; after distillation in a nitrogen current over sodium, the hydrocarbon (yield 66% of the theoretical) showed the following constants:

B.p. 135-136° at 755 mm, n_D^{20} 1.4872, d_4^{20} 0.8308, MR_D 35.83. $C_8H_{12}F_2$. Calculated 36.01.

Literature data [8]: b.p. 135-136°, n_D^{20} 1.4856, d_4^{26} 0.8373.

Addition of hydrogen bromide to 1,3-dimethylcyclohexadiene was conducted under chilling by snow and salt; a current of dry hydrogen bromide was passed through the hydrocarbon until the weight gained corresponded to the addition of one molecule of hydrogen bromide (12-12.5 g). Immediately after the hydrobromide was obtained, it was dissolved in an equal volume of ether and reacted with organomagnesium compounds.

Reaction of 1,3-dimethylcyclohexadiene-1,3 hydrobromide with alkylmagnesium halogenides (RMgX, where $R=CH_3$, C_2H_5, C_3H_7) was effected under the conditions previously described by us for other tertiary allyl bromides [1,2], i.e., under a 1 : 1.5 : 1.5 ratio of hydrobromide, alkyl haloid and magnesium, with constant stirring and chilling of the reaction to –40 or –50°, and subsequent heating and stirring for six hours. The reaction products – cyclohexene hydrocarbons with a quaternary carbon atom – were distilled with sodium into a column with an efficiency of 25 to 30 theoretical plates; the constants of the hydrocarbons produced (not described in the literature*) and their yields are presented in Table 1.

1,3-Dimethyl-1-ethylcyclohexene-2

5.510 mg substance: 17.521 mg CO_2; 6.532 mg H_2O. 2.957 mg substance: 9.412 mg CO_2; 3.460 mg H_2O. Found %: C 86.78, 86.86; H 13.26, 13.09. $C_{10}H_{18}$. Calculated %: C 86.88; H 13.12.

1,3-dimethyl-1-ethylcyclohexene-2 was subjected to Raman spectra study; the basic frequency of the double bond (1677 cm^{-1}) corresponded to the cyclohexene hydrocarbon with double bond to the alkylated carbon atom.

Relation of 1,3-dimethyl-1-ethylcyclohexene-2 to irreversible catalysis. 1,3-dimethyl-1-ethylcyclohexene-2 was passed through platinized charcoal (15% Pt) in a nitrogen current at 200° (conditions of irreversible catalysis [4]). The produced catalysis products discolored bromine water instantaneously and possessed the constants of the initial hydrocarbon. Study of the Raman spectrum of the catalysis products showed a complete absence of the characteristic lines of aromatic hydrocarbons.

Hydrogenation of the synthesized cyclohexene hydrocarbons with aluminum oxide over nickel at 170° resulted in the production of the corresponding cyclohexane hydrocarbons, possessing the constants shown in Table 2.

The data for 1,1,3-trimethylcyclohexane given in the literature are: Knoevenagel [3] b.p. 137-138° (760mm) n 1.4324, d_4^{15} 0.7848; Fenske [7] b.p. 136.63°, n_D^{20} 1.4296.

Table 3 compares the Raman spectra for 1,1,3-trimethylcyclohexane found in the present study with those presented in the literature on that hydrocarbon.

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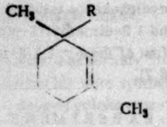
* The activity of the catalyst in irreversible catalysis was verified before and after the 1,3-dimethyl-1-ethylcyclohexene-2 was passed, by passing cyclohexene.

TABLE 1

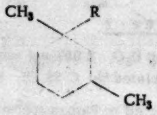
Hydrocarbons of the general structure



R	Name	Boiling points	n_D^{20}	d_4^{20}	MR_D		Yield, % of theoretical
					Found	Calculated	
CH_3	1,1,3-Trimethylcyclohexene-2	137.5-138.8° (757 mm)	1.4583	0.8123	41.67*	42.19	34
C_2H_5	1,3-Dimethyl-1-ethylcyclohexene-2	164-164.4° (757 mm)	1.4593	0.8278	46.13	45.71	27
C_3H_7	1,3-Dimethyl-1-propylcyclohexene-2	181.5-182.5° (755 mm)	1.4632	0.8260	50.69	50.33	13

TABLE 2

Hydrocarbons of the general structure



R	Name	Boiling points	n_D^{20}	d_4^{20}	MR_D	
					Found	Calculated
CH_3	1,1,3-Trimethylcyclohexane	135° (758 mm)	1.4318	0.7808	41.83	41.56
C_2H_5	1,3-Dimethyl-1-ethylcyclohexane**	165-165.5° (758 mm)	1.4419	0.8005	46.27	46.18
C_3H_7	1,3-Dimethyl-1-propylcyclohexane	187-188° (751 mm)	1.4467	0.8065	50.99	50.80

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* The 1,1,3-trimethylcyclohexene-2 produced may contain an impurity in the form of the initial dimethylcyclohexadiene, which distills at almost the same temperature (b. p. 135-136°).

** Not described in the literature.

We used a Steinchel spectrograph with the usual 6cm^{-1} slit to obtain the 1,1,3-trimethylcyclohexane spectrum; the line intensity was measured visually, by means of a conventional scale, in which a frequency intensity of 1450 cm^{-1} was taken as 10 units.

TABLE 3
Spectrum of 1,1,3-trimethylcyclohexane

Obtained in present study	Data from the literature	
	[6]	[7]
224 (0.5), 242 (0.3),		
272 (0.5; w), **325 (6)**.	326 (3),	329 (0.062),
355 (0.1), 376 (0.1),	363 (0),	
399 (1.8), 419 (1.8),	401 (1), 419 (0.5),	402 (0.041),
442 (1), **463 (4)**	437 (0.5), 465 (2)	465 (0.062),
499 (0), 537 (0.3),		499 (0.017),
547 (0.1), **556 (12),**	557 (5),	557 (0.109),
587 (0.1), 621 (0),		
670 (0.5), **726 (20),**	726 (8),	669 (0.014), 728 (0.163),
769 (0), 797 (2),	797 (2),	796 (0.032),
859 (0.5; w), 909 (0.8),	854 (1; w), 910 (1),	853 (0.033), 912 (0.017),
938 (4), 956 (0.3),	937 (2),	937 (0.047),
970 (1.5), **983 (1.5),**	980 (2);	979 (0.047),
996 (0.8), **1046 - 1057** (3; w),	1023 (0.5), 1051 (2),	1048 (0.035),
1079 (8), 1095 (2),	1078 (4),	1080 (0.057),
1117 (0.1), **1138 (2)**,	1136 (1),	1136 (0.008),
1162 (0.5), 1170 (0.5),		
1193 (9), 1219 (4)* .	1193 (3),	1195 (0.071), 1220 (0.052),
1248 (4), 1258 (0),	1247 (3),	1252 (0.040),
1270 (1), 1296 (0.5),	1281 (3),	1290 (0.044),
1309 (1), 1348 (3; w),	1311 (1), 1353 (2),	1313 (0.041), 1359 (0.052),
1440 (5; w), **1460 (10),**	1381 (1), 1440 (5),	1452 (0.156),
	1462 (6),	1464 (0.158).

The data presented in Table 3 show that all lines of maximum and medium intensity in the adduced spectra of 1,1,3-trimethylcyclohexane coincide. A few of the lines of low and medium intensity in our 1,1,3-trimethylcyclohexane spectrum are superimposed upon the intense lines of the isomeric hydrocarbons — 1,2,3-trimethylcyclohexane [325 (3); 418 (8); 539 (7); 975 (6); 1159 (4); 1193 (4); 1315 (6; w)] [6] and 1,2,4-trimethylcyclohexane [416 (3)] [6]. However, the spectrum we obtained lacked other lines of high intensity typical of 1,2,3-trimethylcyclohexane: 734 (7); 833 (4); 921 (4); 1063 (4); 1233 (3); 1278 (3); 1315 (6; w) [6] and of 1,2,4-trimethylcyclohexane: 455 (3); 522 (3); 615 (5); 747 (8) [6], thus confirming the absence of these isomeric hydrocarbons (the possibility of whose formation was discussed above) in the 1,1,3-trimethylcyclohexane synthesized by us.

Below we present the Raman spectra of two other cyclohexane hydrocarbons we have synthesized — 1,3-dimethyl-1-ethyl cyclohexane and 1,3-dimethyl-1-propylcyclohexane; these spectra were taken under the same conditions as that of 1,1,3-trimethylcyclohexane.

1,3-Dimethyl-1-ethylcyclohexane: 193 (0.1; g), 257 (0.2; w), 276 (0.1; w), 322 (3; w), 345 (2.5), 406 (3), 414 (1), 435 (1), 462 (3), 495 (1.5; db) 518 (0.2), 547 (0), 558 (4), 570 (0.5), 663 (0), 700 (1.5), 722 (4; db), 783 (0), 792 (3; db), 795 (3; db), 846 (1.5), 860 (1.5), 875 (1), 895 (0.5), 943 (0.8), 953 (3), 963 (0.3), 978 (1), 991 (2), 1003 (3), 1023 (0), 1046 (1.2), 1068 (1; db), 1082 (4), 1102 (1), 1107 (0.1), 1141 (2), 1162 (1.5), 1194 (5), 1215 (3), 1227 (2), 1259 (1), 1270 (2.5; w), 1307 (0.5; w), 1347 (1), 1350 (2), 1358 (1), 1382 (0.3), 1439 (10), 1460 (10).

1,3-Dimethyl-1-propylcyclohexane: 274 (1; w), 299 (1.8), 314 (1.5), 336 (0.5), 406 (2), 413 (0.1), 444 (0.3), 467 (1.5), 488 (1.5), 504 (1), 525 (0.8), 567 (2.5), 586 (0.4), 734 (5; w), 746 (0), 769 (0), 796 (2), 820 (0.1), 845 (0), 861 (1.5), 896 (1.2; w), 930 (1), 963 (0.5), 985 (0.5), 1015 (0.5), 1040 (1), 1056 (1.5), 1080 (2), 1105 (1.5), 1133 (1.5), 1165 (1.5), 1190 ([illegible].5), 1204 (1.5), 1226 (0.8), 1256 (0.3), 1270 (1), 1294 (0.5), 1310 (1.5), 1354 (8; w); 1382 (0.2), 1440 (9), 1460 (10).

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*The line of medium intensity 1219 cm^{-1} discovered in our spectrum but lacking in Chinerdoglu's [6] was also observed by Fenske [7] in the spectrum of this hydrocarbon.

SUMMARY

1. A new method has been developed for the synthesis of cyclohexane hydrocarbons with two alkyl groups and one carbon atom – 1,3-dimethyl-1-alkylcyclohexenes-2 (alkyl – CH_3, C_2H_5, C_3H_7). This is a three-stage method; 1) synthesis of 1,3-dimethylcyclohexadiene-1,3; 2) hydrobromination of that compound and 3) reaction of the tertiary allyl hydrobromide thus formed with RMgX.

2. The structure of the synthesized cyclohexene hydrocarbons was confirmed by their physical properties, including the Raman spectrum of one of them, and also by their stability under irreversible catalysis, which verified the presence of a quaternary carbon atom in the ring.

3. Hydrogenation of the synthesized hydrocarbons resulted in production of the corresponding cyclohexane hydrocarbons with a quaternary carbon atom – 1,3-dimethyl-1-alkylcyclohexanes.

4. 1,1,3-Trimethylcylcohexene-2, 1,3-dimethyl-1-ethylcyclohexene-2, 1,3-dimethyl-1-propylcyclohexene-2, 1,3-dimethyl-1-ethylcyclohexane and 1,3-dimethyl-1-propylcyclohexane are here described for the first time.

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CATALYTIC ALKYLATION OF BENZENE BY BUTYL ALCOHOL

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The butyl benzenes are usually obtained by two methods: the alkylation of benzene by butylene and isobutylene or the alkylation of benzene by butyl alcohols. These reactions are conducted at atmospheric or elevated pressures, in the liquid phase, in presence of hydrofluoric acid, hydrochloric acid [1,2], boric fluoride [3,4], aluminum chloride [5,6] or other compounds.

In a previous study one of us [7] established the possibility of alkylating benzene with ethyl and propyl alcohols over an aluminum silicate catalyst in a flow system at atmospheric pressure. The present study was the first in which benzene was alkylated by n-butyl alcohol under these conditions. It was established that secondary and n-butyl benzenes are the main reaction products — products of alkylating benzene with butylene. Tertiary butyl benzene is present in the alkylation products only in negligible quantity, and isobutyl benzene is lacking. It follows from this data that isomerization of butylene and isobutylene takes place to only a negligible extent under the conditions of our reaction.

Under optimum conditions, the yield of isomeric butyl benzenes attains 35% of the alcohol used in the reaction.

EXPERIMENTAL

The initial substances used where thiophene-free benzene, b.p. 79.5-80° (755 mm); n_D^{20} 1.5018, d_4^{20} 0.8786 and n-butyl alcohol, b.p. 116-117° (759 mm), n_D^{20} 1.3995, d_4^{20} 0.8095.

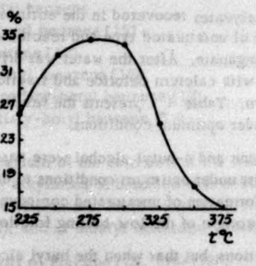

Fig. 1. Butyl benzene yield relative to experiment temperature. Benzene/alcohol ratio is 4 : 1; space velocity 0.66.

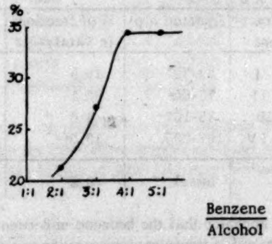

Fig. 2. Butyl benzene yield relative to benzene content of initial mixture. Temperature 300°; space velocity 0.66.

As in the previous study, the alkylation reaction took place in the vapor phase in a flow system at atmospheric pressure over a commercial aluminum silicate catalyst.

Dependence of butyl benzene yield on temperature (Fig. 1), on composition and rate of delivery of the reaction mixture (Figs. 2-3), and on duration of the experiment (Fig. 4) were investigated.

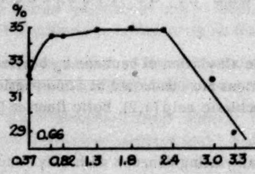

Fig. 3. Butyl benzene yield relative to rate of delivery of reaction mixture.
Benzene/ alcohol ratio is 4 : 1; temperature 300°.

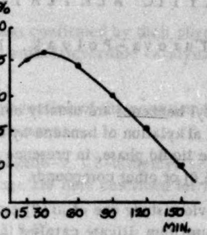

Fig. 4. Butyl benzene yield relative to duration of experiment.
Temperature 300°; benzene/ alcohol ratio is 4 : 1; space velocity 0.66.

These curves show:

1. The optimum temperature of experiment is 275 - 300°. Butyl benzene fraction yield falls steadily with rising temperature.

2. Increasing the benzene content of the reaction mixture to 4 : 1 facilitates a rise in reaction product yield.

3. Butyl benzene fraction yield is virtually constant when the reaction mixture is delivered at a space velocity of between 0.66 and 2.4; further rise in rate of delivery of the mixture brings a reduction in reaction product yield.

4. Butyl benzene fraction yield remains practically constant at durations of experiment between 15 and 60 minutes, but yield falls steadily as duration of experiment increases.

TABLE 1

Fractions	Fraction b.p.	% of fraction in Catalyzate	n_D^{20}
I	32-79*	10.8	1.4630
II	79-85*	63.5	1.4969
III	85-167	4.0	1.4875
IV	167-237	13.5**	1.4895
	losses	8.2	

Catalyzates recovered in the entire series of experiments were of unsaturated type and reacted energetically with permanganate. After the water was driven off, they were dried with calcium chloride and fractionated over metallic sodium. Table 1 presents the results of catalyzates distillation under optimum conditions.

Benzene and n-butyl alcohol were passed separately over catalyst under optimum conditions to discover the reason for the formation of unsaturated compounds in the catalyzates and the origin of the low-boiling fractions (32-79°). It appeared that the benzene underwent no change under these conditions, but that when the butyl alcohol was so passed, a liquid catalyzate was formed, in quantity 41% of the alcohol used in the reaction, and also gaseous products consisting of unsaturated compounds (89.1%), carbon monoxide (0.6%), hydrogen and saturated compounds (10.3%).

After bromine absorption of the gaseous products, bromides were obtained with constants similar to that of the dibromobutanes.

The liquid portion of the catalyzate was unsaturated in character and reacted actively with a solution of permanganate and bromine water. After distillation of the water it was dried and distilled. Distillation findings are presented in Table 2.

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* The excess benzene was distilled off the 79-85° fraction after processing with concentrated sulfuric acid, and then used in the work.

** Yield of this fraction relative to initial alcohol was 34.9%.

No more detailed study of the fractions obtained was undertaken. However, the works of Lebedev [8], Kazansky and Rozengardt [9], Maslyansky [10] and others permit us to postulate that the products of the given reaction were formed as the result of polymerization of butylenes.

The Raman spectrum was used to determine the composition of the butyl benzene fraction boiling over the wide range from 167 to 237° (Table 1). The fraction was first treated with concentrated sulfuric acid, appropriately washed, dried and distilled over sodium into finer fractions (Table 3).

TABLE 2

Fractions	Fraction b.p.	% of fraction in catalyst	n_D^{20}	d_4^{20}	Bromine number	% of unsaturated compounds
I	40°	5.4	1.4036	-	-	-
II	40-70	1.4	-	-	-	-
III	70-100	18.7	1.4040	0.7165	76.5	46.8
IV	100-125	38.6	1.4087	0.7170	82.5	57.7
V	125-150	6.7	1.4210	0.7463	90.7	71.4
VI	150-200•	17.8	1.4540	0.8045	84.8	40.0
	losses	11.6	-	-	-	-

TABLE 3

Butyl benzene fraction under study	Fraction b.p.	Fraction content (% by weight)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
I	167-170°	15.0	1.4890	0.8605	44.95	44.77
II	170-172	52.0	1.4896	0.8612	44.91	44.77
III	172-181	5.8	1.4907	0.8631	45.00	44.77
IV	181-183.5	4.8	1.4909	0.8636	45.00	44.77
V	200-237	14.0	1.4925	0.8646	63.80	63.25
losses	-	8.4	-	-	-	-

TABLE 4

Hydrocarbons	b.p.	n_D^{20}	d_4^{20}
n-Butyl benzene [11]	182-183.1°	1.4880	0.8668
tertiary Butyl benzene	168.5-169.5[14]	1.4919 [15]	0.8665 [15]
secondary Butyl benzene [12]	172.5	1.4898	0.8608
Isobutyl benzene [12]	170.1	1.4928	0.8673
1,4-Di-n-butyl benzene [12]	259 (745 mm)	1.4879	0.8556
1,4-Di-secondary-butyl benzene [12]	237.0	1.4878	0.8573
1,4-Di-tertiary-butyl benzene [12]	237 (m.p.77°)	1.4624 (90°)	0.8659

Comparison of the constants of the individual butyl benzenes (Table 4) with those of the butyl benzene fractions obtained by alkylation of benzene with n-butyl alcohol (Table 3) shows that the alkylation product consisted chiefly of a mixture of isomeric butyl benzenes (77.6%) (Fractions I-IV) with a predominance of secondary butyl benzenes (Fraction II), and of dibutyl benzenes, constituting approximately 14% (Fraction V).

Analysis of Fraction (II), 170-172°.

7.335 mg sub.: 24.105 mg CO_2; 6.930 mg H_2O. 7.305 mg sub.: 24.000 mg CO_2; 6.838 mg H_2O. Found %: C 89.68, 89.66. H 10.57, 10.48. $C_{10}H_{14}$. Calculated %: C 89.52; H 10.51.

All fractions, except that between 200 and 237°, were subjected to Raman spectrum study. The bright lines of all fractions studied fell within a narrow range.

The spectrums of the 167-170° and 170-172° fractions were identical in brightness and frequency of Raman spectrum lines.

Spectra of fractions 167-170° and 170-172°: 229 (1; w); 280 (0.8); 311 (2.5); 333 (3); 461 (7); 546 (0.5); 559 (2);

• The small quantity of substance made it impossible to determine the limits of boiling accurately.

588 (1.5); 619 (12); 702 (1); 732 (12); 746 (2.5); 764 (2); 792 (1.5); 808 (2.5); 843 (2); 856 (2.5); 903 (1.5); 929 (0.5); 948 (2.5); 956 (2); 987 (1); 1000 (1.5); 1002 (80); 1034 (25); 1056 (2); 1085-1117 (2; w); 1160 (7); 1189 (6); 1206 (2); 1239 (0.5); 1258 (0.5); 1272 (1.5); 1296 (1); 1323 (0.5); 1335 (1); 1353 (1); 1382 (1); 1397 (1); 1443 (2); 1460 (10); 1584 (4); 1608 (20).

Comparison of the spectra obtained with those for n-butyl benzene, secondary, tertiary and isobutyl benzenes obtained by Genske [13], shows that the fractions studied constituted a mixture of secondary butyl benzene (primarily) with n- and tertiary butyl benzene. The presence of secondary butyl benzene was determined by the brightest lines in the spectrum: 311, 461, 619, 732, 746, 903, 1002, 1034, 1206.

The presence of n-butyl benzene was established by spectral lines 229, 280, 1056, 1296, while the other n-butyl benzene lines were superimposed upon those of secondary butyl benzene. Tertiary butyl benzene is characterized by spectral lines 702 and 929.

The brightness of the lines of the Raman spectra was not measured photometrically, but visually.

In terms of the data of spectrographic analysis, the content of isomeric butyl benzenes in the fractions under study was approximately the following: secondary butyl benzene 85-90%, n-butyl benzene 10-12%, tertiary butyl benzene — negligible. If isobutyl benzene was present, it could only have been in trace quantity.

The spectrum of the 181-183.5° fraction is very similar to that of the 167-170° fraction. It consists of a mixture of secondary butyl benzene and n-butyl benzene, with a very insignificant admixture of tertiary butyl benzene.

Spectrum of the 181-183.5° fraction: 229 (2); 284 (1.5); 310 (1.8); 333 (1); 405 (0); 462 (2.5; w) 501 (1.5); 565 (1); 598 (1); 612 (10); 701 (0.3); 735 (10); 746 (0.8); 762 (0.8); 792 (0.8); 810 (1.5); 843 (1); 857 (1,5); 904 (2); 948 (2); 956 (0.8); 974 (0.5); 1002 (50); 1034 (20); 1057 (1); 1085 (1.5;); 1117 w); 1157 (5); 1182 (3); 1206 (12); 1241 (0.3); 1286 (1.5; w); 1296 (1.5); 1323 (0.3; g); 1347 (0.5); 1382 (0.3); 1453 (10); 1608 (18).

The presence of secondary butyl benzene was established in terms of lines: 310, 462, 621, 735, 746, 904, 1002, 1034, 1206; and n-butyl benzene by lines: 229, 284, 501, 565, 1057, 1296. Tertiary butyl benzene is characterized by line 701.

The quantitative composition of the fractions was approximately as follows: secondary butyl benzene ~75-78%, n-butyl benzene ~ 22-25%, tertiary butyl benzene — traces; isobutyl benzene was lacking.

SUMMARY

1. Alkylation of benzene by n-butyl alcohol in a flow system at atmospheric pressure was performed for the first time.

2. Alkylation resulted in the formation of a mixture of butyl benzenes, with secondary butyl benzene predominating.

3. The optimal conditions for production of butyl benzenes must be considered to be a temperature of 300°, and a molar ratio of 4 : 1 between benzene and n-butyl alcohol; a volumetric velocity of delivery of the reaction mixture of 0.66-2.4; under these conditions the butyl benzene yield attains 35% of the alcohol used in the reaction.

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CONTACT CONVERSIONS OF BUTYLCYCLOHEPTANE IN THE PRESENCE OF PLATINIZED CHARCOAL

S. I. Khromov, E. S. Balenkova and B. A. Kazansky

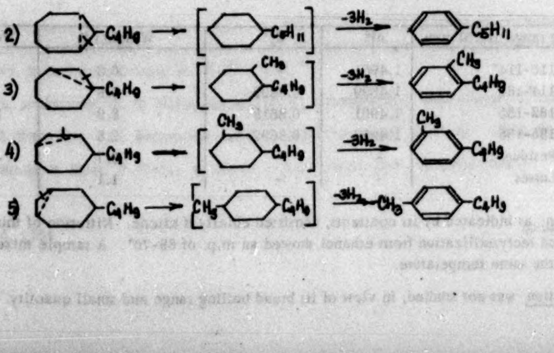
We have previously shown [1], from study of catalytic conversions of certain alkyl and aryl cycloheptanes over platinized charcoal under conditions of catalytic dehydrogenation that these hydrocarbons withstand isomerization of the hepta to the hexa cycle with formation of semi-substituted cyclohexane hydrocarbons.

Thus, for example, phenylcycloheptane, the simplest cycloheptane aryl derivative, placed in contact with platinized charcoal at 320°, gives about 7% semi-methylphenylcyclohexane; the alkylcycloheptanes (methyl, ethyl- and propylcycloheptanes) will yield up to 28% of semi-methylalkylcyclohexanes.

In the development of the previously described cases of isomeric conversion of heptamethylene hydrocarbons it appeared to us to be of interest to study the behavior of butylcycloheptane under conditions of catalytic dehydrogenation. With this object we synthesized butylcycloheptane, and put this hydrocarbon in contact with 10% platinized charcoal at 320°. The catalyzate (for separation of naphthene hydrocarbons from the aromatics) was subjected to chromatographic adsorption on silica gel. The naphthene portion of catalyzate produced by chromatographic adsorption consisted chiefly of 1-methyl-1-butylcyclohexane (semi-methylbutylcyclohexane). The aromatic portion of the catalyst obtained by chromatographic adsorption on silica gel, was distilled in a column of 15 theoretical plates. The composition of the separate fractions of the aromatic part of the catalyzate was determined by oxidation with an aqueous solution of potassium permanagate [2].

On the basis of the research results obtained, the approximate proportions of hydrocarbons in the total mass of catalyzate of butylcycloheptane contact conversion, in %, is as follows: about 29% 1-methyl-1-butylcyclohexane; 32% butylbenzene; 25% o-methylbutylbenzene; 6% m-methylbutylbenznee, 4% p-methylbutylbenzene, 3% amylbenzene, and 1% toluene.

The contact conversions of butylcycloheptane may be expressed by the following reaction scheme:



The production of butylbenzene and toluene among the reaction products of catalytic conversion of butylcycloheptane is apparently to be ascribed to the occurrence of a secondary process – the catalytic conversion of 1-methyl-1-butylcyclohexane formed in the course of the main reaction. In our experience, as in the cases of catalytic conversion of alkyl and aryl cycloheptanes previously studied, the disruption of the hepta ring during isomerization into hexa ring occurs primarily through a single carbon atom from carbon with alkyl substitutes.

EXPERIMENTAL

Synthesis of butylcycloheptane. 1-Butylcycloheptanol-1 was obtained from suberone and butylmagnesium bromide. The alcohol was dehydrated in presence of iodine, and the 1-butylcycloheptene-1 thus formed was hydrogenated in presence of platinized charcoal to butylcycloheptane. To eliminate the traces of the unsaturated hydrocarbon the butylcycloheptane was subjected to chromatographic adsorption over silica gel, and then vaccum distilled in a column.

B. p. 80.0° (10mm), 207.4° (755 mm), n_D^{20} 1.4517, d_4^{20} 0.8195; MR_D 50.65. $C_{11}H_{22}$. Calculated. 50.79.

9.629 mg. sub.: 30.249 mg CO_2; 12.315 mg H_2O. 8.170 mg sub.: 25.266 mg CO_2; 10.510 mg H_2O. Found %: C 85.74, 85.72; H 14.30, 14.39. $C_{11}H_{22}$. Calculated %: C 85.63; H 14.37.

Butylcycloheptane is not described in the literature.

Contact conversion of butylcycloheptane. 60 ml of 10% platinized coal was placed in a catalytic tube, and 40 g butylcycloheptane was passed over the catalyst at 320°, with a volumetric velocity of 0.2. The results are shown in Table 1.

TABLE 1

Pass	n_D^{20}	Gas liberated (ml)	Catalyzate obtained, wt (g)
1	1.4728	10360	35.4
2	1.4725	3590	34.2
3	1.4802	1050	33.7
4	1.4816	790	33.4
	Total......	15790	-

The gaseous catalysis products were analyzed with a V. T. I. apparatus. The results of gas analysis in %: H_2 86.8; C_nH_{2n+2} 12.7.

Study of the Catalyzate. The catalyzate obtained by contact conversions of butylcycloheptane for separation of naphthene hydrocarbons from the aromatic hydrocarbons formed during catalysis, was subjected to chromatographic adsorption on silica gel. The naphthene fraction (9.5 g) evolved by this method of dissociation boiled at 191-191.5° (763 mm), n_D^{20} 1.4477, d_4^{20} 0.8129, MR_D 50.63. $C_{11}H_{22}$. Calc. 50.79.

The constants of the 1-methyl-1-butylcyclohexane previously synthesized by us were [3]: b.p. 191.5° (758 mm), n_D^{20} 1.4477, d 0.8137.

To confirm the presence of 1-methyl-1-butylcyclohexane in the catalysis products, the naphthene portion of the catalyst was also studied by the Raman spectrum method. Comparison of the spectrum of the naphthene portion of the butylcycloheptane catalyzate studied with that of pure 1-methyl-1-butylcyclohexane demonstrated their identity.

The aromatic portion of the catalyzate (23.4 g) was subjected to fractionation in a column. Table 2 presents the results of this distillation.

Distillation of the residue in a small retort gave a fifth fraction, 9.4 g in quantity, boiling at 195-203° (751 mm), n_D^{20} 1.4990, d_4^{20} 0.8742.

TABLE 2

Fraction No.	Boiling range at 751 mm	n_D^{20}	d_4^{20}	Weight (g)	Weight, %
1	110-114°	1.4961	-	0.3	1.3
2	114-182	1.4899	0.8609	0.8	3.4
3	182-185	1.4901	0.8618	8.9	38.0
4	185-195	1.4926	0.8692	2.6	11.1
	Residue	-	-	9.7	41.5
	Losses	-	-	1.1	4.7

The first fraction, as indicated by its constants, consisted chiefly of toluene. Nitration of this fraction gave a nitro product which, upon recrystallization from ethanol, showed an m.p. of 69-70°. A sample mixed with pure 2,4-dinitrotoluene melted at the same temperature.

The second fraction was not studied, in view of its broad boiling range and small quantity.

3rd Fraction. 2.5 g of the third fraction was oxidized by an aqueous potassium permanganate solution. Oxidation gave 2.12 g benzoic acid, m.p. 120.5°.

Comparison of the third fraction constants with those in the literature on butylbenzene made it possible to conclude that it consisted chiefly of that compound.

Data on butylbenzene in the literature [4]: b.p. 183.35 (760 mm), n_D^{20} 1.4897, d_4^{20} 0.8608.

The fact that oxidation of the third fraction gave only benzoic acid completely confirmed the fact that the fraction consisted solely of butylbenzene.

4th Fraction. Oxidation of 2.6 g of this fraction gave the following acids: benzoic (0.12 g), orthophthalic (0.33 g), isophthalic (0.45 g) and terephthalic (0.38 g).

5th Fraction. Oxidation of 6.0 g of the fifth fraction revealed the following acids: benzoic (0.30 g), orthophthalic (2.29 g), isophthalic (0.32) and terephthalic (0.15 g).

The presence of benzoic acid in the oxidation products of the 5th fraction (and partially of the 4th) is to be ascribed to the oxidation of amylbenzene, and not butylbenzene, as the boiling point of the latter is considerably below the distillation range of the fifth fraction. Formation of phthalic acids in the 4th and 5th fractions must be ascribed to oxidation of the o-, m- and p-methylbutylbenzenes.

Table 3 presents a typical composition of the aromatic portion of butylcycloheptane catalyst, computed in terms of chemical analysis and the physical constants of the fractions obtained.

TABLE 3

Fraction No.	Boiling range, 751 mm	Weight (g)	% of total aromatic hydrocarbons	percentage content of					
				toluene	butylbenzene	methylbutylbenzenes			amylbenzene
						ortho	meta	para	
1	110-114°	0.3	1.3	1.3	-	-	-	-	-
2	114-182	0.8	3.6	-	3.6	-	-	-	-
3	182-185	8.9	40.4	-	40.4	-	-	-	-
4	185-195	2.6	11.9	-	1.0	2.9	4.0	3.5	0.5
5	195-203	9.4	42.8	-	-	32.6	4.4	2.1	3.7
	Total....	22.0	100.0	1.3	45.0	35.5	8.4	5.6	4.2

SUMMARY

1. n-Butylcycloheptane was synthesized and described for the first time.

2. The contact conversions of butylcycloheptane in presence of platinized charcoal at 320° were studied, and it was established that they result in the formation of considerable quantities of 1-methyl-1-butylcyclohexane and mixtures of aromatic hydrocarbons consisting of toluene, butylbenzene, o-, m- and p-methylbutylbenzenes.

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BROMINATION OF 1,1-DIPHENYLETHANE

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Continuing the study of the halogenation of 1,1-diphenylethane undertaken by one of us [1], we investigated its bromination reaction. This reaction was been described by Scheibly and Prutton [2]. These authors reacted 1,1-diphenylethane with various quantities of bromine in the light, at 100°. A very insignificant quantity of stilbene was separated out upon distillation of the reaction mixture and, in another case, some 1,1,4,4-tetraphenylbutadiene-1,3. The main bromination product was an oil which these authors did not study at all.

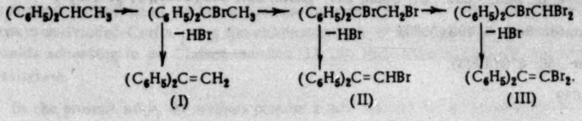
We brominated 1,1-diphenylethane, produced from acetylene and benzene [3] in a quartz flask lit by an electric bulb, at 100 to 200°. Gradual addition of bromine resulted in an energetic reaction with heavy production of hydrogen bromide. The products were separated by distillation, followed by crystallization.

The results varied with the bromine consumption. When 1.3 mole of bromine was used per 1 mole of 1,1-diphenylethane, the product was 1,1-diphenylethylene (I) with a yield of 70% of the theoretical, plus a small amount (12%) of 1,1-diphenyl-2-bromethylene (II).

When 2 mole of bromine was used, the result was a readily crystallized oil, from which the following were obtained: (II) (63%) and 1,1,-diphenyl-2-2-dibromethylene (III) (12%). The latter was the sole product when 3 mole of bromine was used; it was obtained in a yield of 84% of the theoretical.

Identification of (III) was performed by means of the Goldschmidt reversible reaction [4]. Identification of (II) was by conversion to tolane by fusion with an alkali [5]. Further, (II) was synthesized from 1,1-diphenylethylene [5].

Thus, the following products may be obtained from 1,1-diphenylethane, depending upon the quantity of bromine:



$$\begin{tikzcd}
(C_6H_5)_2CHCH_3 \arrow[r] & (C_6H_5)_2CBrCH_3 \arrow[r] \arrow[d, "-HBr"] & (C_6H_5)_2CBrCH_2Br \arrow[r] \arrow[d, "-HBr"] & (C_6H_5)_2CBrCHBr_2 \arrow[d, "-HBr"] \\
 & (C_6H_5)_2C{=}CH_2 & (C_6H_5)_2C{=}CHBr & (C_6H_5)_2C{=}CBr_2
\end{tikzcd}$$

(I) (II) (III)

It is apparent that the reactions proceed by the substitution of one, two or three of the ethane hydrogens by bromine, and the subsequent liberation of hydrogen bromide. We made repeated attempts to isolate the primary products. With this object, the reaction was performed at the lowest possible temperatures (30-80°), and the raw mixture was not subjected to distillation. Crystallization of the resultant oil was not successful in a single instance. These oils probably consist of a mixture of saturated and unsaturated bromides.

Our results differ sharply from those obtained by Scheibly and Prutton [2]. We attempted in several experiments, in which we adhered to all the conditions set forth by these authors, to obtain 1,1,4,4-tetraphenylbutadiene-1,3. Invariably, however, the results of bromination failed to differ from those adduced above. It is possible that this discrepancy may be explained by the inadequate purity of the 1,1-diphenylethane employed by Scheibly and Prutton.

EXPERIMENTAL

1,1-Diphenylethylene (I). 20 g (0.11 mole) 1,1-diphenylethane (b.p. 265-270° at 730 mm) was placed in an open quartz flask illuminated by a 500-watt lamp. A thermometer and the bottom of a dropping funnel from which the bromine was delivered were placed in the above liquid. 7 ml (0.14 mole) bromine was added in the course of an hour, the temperature of the mixture being maintained within the range of 160-200°. 19.3 g of the raw product, showing a b.p. of 270-310°, was obtained. Repeated distillation in a vacuum gave 14 g (about 70%) 1,1-diphenylethylene, b.p. 140-143° (6 mm), and 3.4 g 1,1-diphenyl-2-bromoethylene (II), b.p. 160-170° (6 mm).

To remove the bromine residue, the 1,1-dephenylethylene was agitated with molecular silver and fractionated over sodium. The isolated pure product showed constants in complete correspondence with the data presented in the literature [6]:

B.p. 133.0° (6 mm), d_4^{20} 1.0260, n_D^{20} 1.6014, MR_D 60.22; calc. 59.30.

Bromination in a chloroform solution gave 1,1-diphenyl-2-bromethylene (II) with m.p. 40° [5].

1,1-Diphenyl-2-bromoethylene (II). 14 ml (0.28 mole) bromine was added in the course of an hour to 20 g 1,1-diphenylethylene. 24 g oil, b.p. 290-325°, was liberated. The oil crystallized upon cooling. It gave 4.5 g (12%) 1,1-diphenyl-2,2-dibromethylene, m.p. 83° (from alcohol). After repeated distillation, the remaining oil gave pure 1,1-diphenyl-2-bromoethylene (II), m.p. 40°. The yield was 18 g (63%).

1 g 1,1-diphenyl-2-bromoethylene was fused with 2 g caustic potash [5]. This gave 0.6 g (90%) tolane, m.p. 60°.

1,1-Diphenyl-2,2-dibromethylene (III). As described above, 10 g (0.06 mole) 1,1-diphenylethane was brominated with 10 ml bromine (0.19 mole). This gave 15 g (83.5%) of a completely crystallizing product. Recrystallization from alcohol resulted in isolation of pure 1,1-diphenyl-2,2-dibromethylene (III), m.p. 83-83.5°. An attempt to mix it with the synthesized product by the accepted method [4] did not result in depressing the m.p. Oxidation of the chromium anhydride produced benzophenone, m.p. 47-48°, while its semicarbazone had an m.p. of 166°.

SUMMARY

1. Bromination of 1,1-diphenylethane under light proceeds, with elevation of temperature, to substitution of ethane hydrogens and subsequent liberation of hydrogen bromide

2. Depending upon the quantity of bromine used, the following products are readily produced, with good yields: 1,1-diphenylethylene, 1,1-diphenyl-2-bromethylene and 1,1-diphenyl-2,2-dibromethylene.

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* T. p. = C. B. Translation pagination.

ACYLHYDROXYSILANES IN THE SYNTHESIS OF KETO ACIDS OF THE AROMATIC SERIES

Yu. K. Yuryev, G. B. Elyakov and Z. B. Belyakova

Keto acids of the aromatic series have been adequately studied. Of the numerous existing methods for their synthesis we might single out the Gustavson-Friedel-Crafts reaction, where the anhydrides or chloroanhydrides of dibasic acids are used as the acylating agent. The latter, however, are not so convenient since reaction with them proceeds in two directions, and the corresponding diketone results in addition to the keto acid.

By acylation of benzene with succinic anhydride, β-benzoylpropionic acid [1,2,3] was obtained, by acylation with phthalic anhydride, o-benzoylbenzoic acid [4,5] resulted; by acylation with glutaric and sebacic acid chloroanhydrides, Auger [6], and later Borsche and Wollemann [7,8] obtained γ-benzoylbutyric acid and θ-benzoylpelargonic acid, respectively.

Among other synthetic methods for aromatic keto acids can be indicated, for example, the reaction of dibasic acid anhydrides with organomagnesium compounds [9]. This reaction does not proceed in a well-defined manner, and side products are obtained in addition to the keto acid.

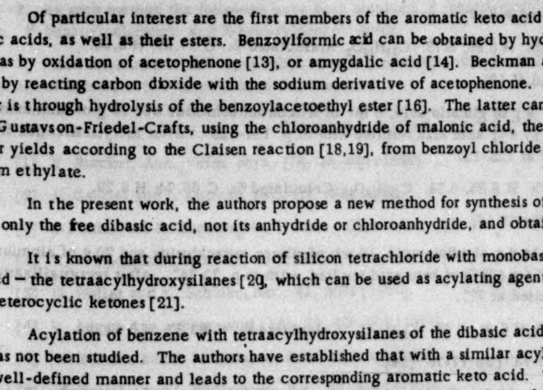
Ketone split of the corresponding α-benzoylsubstituted ester of dibasic acids can also serve as a synthetic method for aromatic keto acids [10,11].

Of particular interest are the first members of the aromatic keto acid series – benzoylformic and benzoylacetic acids, as well as their esters. Benzoylformic acid can be obtained by hydrolysis of benzoyl cyanide [12], as well as by oxidation of acetophenone [13], or amygdalic acid [14]. Beckman and Paul [15] obtained benzoylacetic acid by reacting carbon dioxide with the sodium derivative of acetophenone. A simpler procedure for obtaining the latter is through hydrolysis of the benzoylacetoethyl ester [16]. The latter can be obtained according to the method of Gustavson-Friedel-Crafts, using the chloroanhydride of malonic acid, the ethylester of the acid [17], or in better yields according to the Claisen reaction [18,19], from benzoyl chloride and ethyl acetate in the presence of sodium ethylate.

In the present work, the authors propose a new method for synthesis of keto acids of the aromatic series, using only the free dibasic acid, not its anhydride or chloroanhydride, and obtaining good results.

It is known that during reaction of silicon tetrachloride with monobasic acids reactive compounds are formed – the tetraacylhydroxysilanes [20], which can be used as acylating agents for the synthesis of aromatic [20] and heterocyclic ketones [21].

Acylation of benzene with tetraacylhydroxysilanes of the dibasic acids in the presence of aluminum chloride has not been studied. The authors have established that with a similar acylation of benzene, reaction proceeds in a well-defined manner and leads to the corresponding aromatic keto acid. The reaction mechanism, as well as the structure of the intermediate reaction product – the acylhydroxysilane of the dibasic acid – requires further study.



By such means the authors obtained in good yields β -benzoylpropionic, γ -benzoylbutyric, δ - benzoylvaleric, θ -benzoylpelargonic and o-benzoylbenzoic acids.

It should be mentioned that no positive results were obtained with oxalic acid. On introduction of malonic acid into the reactions, acetophenone resulted; upon acylation with ethyl malonate, the benzoylacetoethyl ester was obtained, and along with it, ethylbenzene.

EXPERIMENTAL

Working Procedure. 0.05-0.1 mole of dibasic acid, 500 ml of dry benzene and 0.09 mole of silicon tetrachloride were introduced into three-necked flask equipped with mechanical stirrer and reflux condenser protected from moisture by a calcium chloride tube. The reaction mixture was heated on a water bath first at 60-80°, and then on a boiling water bath with vigorous stirring to complete cessation of hydrogen chloride evolution.

0.15 mole of anhydrous aluminum chloride was introduced by portions into the pre-cooled mixture with stirring. There was no noticeable reaction in the cold, but with heating on a water bath at 60-70° (thermometer in bath) evolution of hydrogen chloride began, and the reaction mixture became brown or brown-gray in color. Reaction was carried out to completion, heating 2-3 hours on a boiling bath, the reaction flask then cooled with ice, and decomposed with ice water, color usually disappearing, evidently due to decomposition of the complex. Excess benzene was distilled off with water vapor, and the residue transferred to a beaker and acidified with concentrated hydrochloric acid with ice cooling. The precipitate was separated, washed with ice water, transferred to a beaker with a solution composed of 50 g of sodium carbonate in 150 ml of water, and boiled for 10-15 minutes. The hot solution was filtered (if colored it was treated with charcoal) and the keto acid isolated from the filtrate by acidification with concentrated hydrochloric acid.

The keto acids which resulted were usually sufficiently pure; they were recrystallized from water or dilute alcohol.

β -Benzoylpropionic Acid. 11.8 g of succinic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 9 g (51%) of keto acid resulted with m.p. 114-155°. After recrystallization from water, the β -benzoylpropionic acid melted at 116°.

Found %: C 67.81, 67.88; H 5.86, 5.73. $C_{10}H_{10}O_3$. Calculated %: C 67.39; H 5.65.

Literature data: m.p. 116.5° [3].

γ -Benzoylbutyric Acid. 6 g of glutaric acid, 8 ml of silicon tetrachloride and 10 g of aluminum chloride in 309 ml of dry benzene. 5 g (57.5%) keto acid resulted with m.p. 124-125°. After recrystallization from water, the γ -benzoylbutyric acid melted at 126-127°.

Found %: C 69.14, 69.20; H 6.35, 6.34. $C_{11}H_{12}O_3$. Calculated %: C 68.74; H 6.29.

Literature data: m.p. 125-126 [6].

δ -Benzoylvaleric Acid. 14.6 g of adipic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 13.6 g (68%) of keto acid resulted, with m.p. 73.74°. After recrystallization from water, δ -benzoylvaleric acid melted at 77°.

Found %: C 70.28, 70.20; H 6.91, 6.93, $C_{12}H_{14}O_3$. Calculated %: C 69.87; H 6.84.

Literature data: m.p. 72-73° [3]; 77-78° [22].

θ -Benzoylpelargonic Acid. 10.1 g of sebacic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 10.5 g (80%) of keto acid resulted with m.p. 75-78°. After recrystallization from dilute alcohol, the θ -benzoylpelargonic acid melted at 82°.

Found %: C 73.37, 73.41; H 8.65, 8.60. $C_{16}H_{22}O_3$. Calculated %: C 73.26; H 8.45.

Literature data: m.p. 77-79° [6], 85-86° [7].

2-Benzoylbenzoic Acid. 8.3 g of phthalic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 11.8 g (96%) of keto acid resulted with m.p. 91-92°. The keto acid was in the form of a crystalline hydrate with 1 molecule of water. Anhydrous 2-benzoylbenzoic acid with m.p. 127° resulted after recrystallization from xylene.

Found %: C 74.21, 74.26; H 4.62, 4.59. $C_{14}H_{10}O_3$. Calculated %: C74.31; H 4.45.

Literature data: m.p. of the crystalline hydrate was 93-94° [23-24], m.p. of the anhydrous keto acid was 127° [23].

Benzoylethyl Acetate. Obtained by use of milder conditions for the reaction and separation. The silicoanhydride was obtained in similar fashion as described for monobasic acids [21] – from 9 g of freshly-distilled ethyl malonate and 6 g of silicon tetrachloride in 200 ml of anhydrous benzene. 10 g of aluminum chloride was added in portions over a half-hour (the complex forming was red in color). It was heated on a water bath for 4 hours; bath temperature should not exceed 80°. After decomposition with ice water, the reaction mixture was filtered, the benzene layer separated, washed with 2 N sulfuric acid [17], and then washed with water. The aqueous solution was extracted with ether. The benzene-ether extracts were dried with anhydrous magnesium sulfate, and the solvents then distilled off in vacuo and the residue then fractionated.

4.3 g (33%) of benzoylethyl acetate resulted:

B. p. 148-150° (12 mm), n_D^{20} 1.5145, d_4^{20} 1.114. MR_D 52.02. $C_{11}H_{12}O_3\lceil_3$. Calc. 52.10.

Found %: C 68.32, 68.29; H 6.45, 6.39. $C_{11}H_{12}O_3$. Calculated %: C 68.74; H 6.29.

The compound gave an intense red-violet coloration with iron.

Literature data: b.p. 132-137° (4 mm), 165-169° (20 mm) [19]; 159-165° (18 mm) [18].

In addition to the benzoylacetic ester, ethyl benzene was also isolated from the reaction product in the amount of 2.2 g, having the following constants: b.p. 135° (745 mm), n_D^{20} 1.4961, d_4^{20} 0.868.

Acetophenone. Obtained in 44% yield of theory from 10.4 g of malonic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. The b.p. was 200-204°; n_D^{20} 1.5345, d_4^{20} 1.036.

SUMMARY

1. A new synthetic method is proposed for aromatic keto acids – the acylation of benzene with the silicoanhydrides of dibasic acids – which permits use of the dibasic acids themselves in the reaction.

2. By such method the following have been prepared: β-benzoylpropionic, γ-benzoylbutyric, δ-benzoylvaleric, θ-benzoylpelargonic and 2-benzoylbenzoic acids.

3. From the example of benzoylethyl acetate preparation, the possibility for acylation of the benzene ring with the aid of dibasic acid esters has been demonstrated.

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BARBITURIC ACIDS

II. SYNTHESIS OF METHYLENE-BIS-5-ALKENYLBARBITURIC ACIDS

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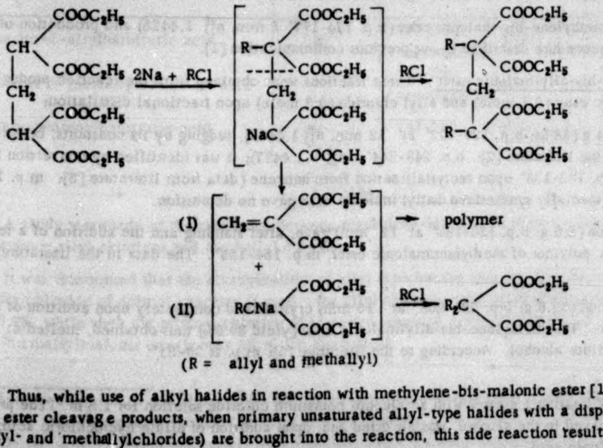
In a previous communication [1] the synthesis of methylene-bis-5-alkylbarbituric acids from methylene-bis-alkylmalonic esters was described. It was established that alkylation of methylene-bis-malonic ester by halide alkyls (in the synthesis of the methylene-bis-alkylmalonic esters) is accompanied by partial dissociation of the intermediate reaction product – the sodium derivative of the monoalkylated methylene-bis-malonic ester – with the formation of methylenemalonic (I) and sodium alkylmalonic (II) esters.

This side reaction proceeds at a yield of 11 to 32% of the theoretical, when primary halides of normal structure (RX = CH_3Br, C_2H_5Br, C_3H_7Br and C_4H_9Br) are used, and at 58-61% for primary halides of the iso structure (RX = iso-C_4H_9Br; iso-$C_5H_{11}Br$).

When benzyl chloride is used, the sodium benzylmalonic ester (II) formed reacts further with benzyl chloride to form dibenzylmalonic ester.

The present work studied the substitution reaction of displaceable α-carbons by unsaturated allyl-type radicals in methylene-bis-malonic ester.

When allyl chloride was reacted with methylene-bis-sodium malonic ester, the normal reaction product was obtained at a yield of 30.6% of the theoretical, while the reaction side product (diallylmalonic ester) was obtained at a yield of 58.7%. When the primary unsaturated chloride of branched structure, methallylchloride, was used, the side reaction went even further (87.2%), similarly to what had occurred with the primary alkyl halides of iso-structure; the main reaction product was dimethallylmalonic ester; methylene-bis-methallylmalonic ester was obtained at a yield of only 5% of the theoretical.

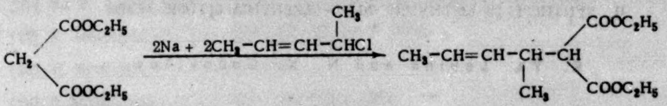


(R = allyl and methallyl)

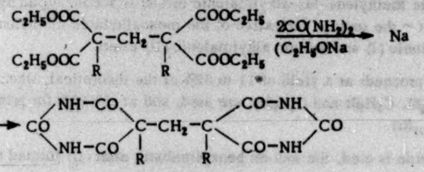
Thus, while use of alkyl halides in reaction with methylene-bis-malonic ester [1] results in monoalkylated malonic ester cleavage products, when primary unsaturated allyl-type halides with a displaceable halide atom (benzyl-, allyl- and methallylchlorides) are brought into the reaction, this side reaction results in the formation of disubstituted malonic esters.

Diallyl- and dimethallylmalonic esters were also directly synthesized from malonic ester. In order to identify these esters, obtained during reaction by cleavage from methylene-bis-malonic ester, they were hydrolyzed into their homologous acids: sample mixtures of these acids with known diallyl- and, correspondingly, dimethallylmalonic acid gave no depression upon melting.

It is necessary to note that an attempt to obtain disecondary pentenylmalonic ester by action of piperylene hydrochloride (a secondary chloride of the allyl type) upon sodium malonic ester under the same conditions which permitted ready synthesis of diallyl- and dimethallylmalonicesters gave, as reaction product, mono-secondary pentenylmalonic ester (penten - 2-yl-malonic ester):

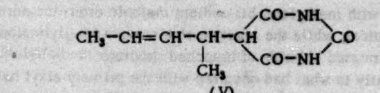


The synthesized methylene-bis-allyl and methylene-bismethallylmalonic esters were converted by action of urea in presence of sodium ethylate into the homologous methylene-bis-5-alkenylbarbituric acids:



[R = allyl (III) and methallyl (IV)].

The secondary pentenylmalonic ester also gave the homologous 5-alkenylbarbituric acid (V):



(V)

EXPERIMENTAL

Alkylation of methylene-bis-malonic ester (b.p. 174-177°, 5 mm, n_D^{20} 1.4425) and production of the barbituric acids followed the procedure described in our previous communication [1].

1. Methylene-bis-allylmalonic ester. Three fractions were obtained from the reaction product of methylene-bis-sodium malonic ester (0.1 mole) and allyl chloride (0.3 mole) upon fractional distillation:

1st fraction [14 g (58%); b.p. 120-122° at 12 mm, n_D^{20} 1.4468], judging by its constants, constituted diallylmalonic ester; (data in the literature [2]: b.p. 243-244°; $n_D^{15.3}$ 1.4477); it was identified by conversion into diallylmalonic acid* with m.p. 132-133° upon recrystallization from benzene (data from literature [3]: m.p. 132-133°). A sample mixture with specially synthesized diallyl malonic acid gave no depression.

The 2nd fraction (2.5 g; b.p. 130-180° at 12 mm) gave, after standing and the addition of a few drops of ether, 1.9 g (11.1%) of a polymer of methylenemalonic ester, m.p. 154-155°. The data in the literature [4] are m.p. 154-156°.

The third fraction (12.6 g; b.p. 201-203° at 10 mm) crystallized completely upon addition of dilute alcohol and cooling with dry ice. The methylene-bis-allylmalonic ester (yield 30.6%) thus obtained, melted at 30-31°, after recrystallization from dilute alcohol. According to the literature [5]: m.p. is 30-31°.

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* Hydrolysis consisted of heating 1 g ester with an alcohol potassium chloride solution for 1.5 hr. The precipitated potassium salt, not dissolved in the alcohol, was air dried and, upon addition of dilute hydrochloric acid, gave 0.45 g (69%) diallylmalonic acid.

2. Methylene-bis-methallylmalonic ester. After fractional distillation, the reaction product of methylene-bis-sodium malonic ester (0.1 mole) and methallyl chloride (0.3 mole), gave the following 3 fractions:

The 1st fraction [23 g (85%); b.p. 115-116° and 5 mm, n_D^{20} 1.4537] judging by its constants, consisted of dimethylmalonic ester; (data in the literature [6]: b.p. 114-116° at 1 mm, n_D^{25} 1.4532); it was hydrolyzed as described above into dimethallylmalonic acid, m.p. 176-177°, after recrystallization from bnezene (yield 50%, not described in the literature). A sample mixed with specially synthesized dimethallylmalonic acid melted without depression.

8.320 mg sub.: 19.053 mg CO_2; 5.695 mg H_2O. 7.145 mg sub.: 16.393 mg CO_2; 4.870 mg H_2O. Found %: C 62.44, 62.39; H 7.64, 7.65. $C_{11}H_{16}O_4$. Calculated %: C 62.26; H 7.59.

The second fraction (4.7 g; b.p. 160-173° at 5 mm), upon addition of ether, gave 3.5 g (20%) of a polymer of methylenemalonic ester (m.p. 155-156°).

The third fraction (6.7 g; b.p. 203-207° at 7 mm), upon addition of dilute alcohol and cooling with dry ice gave 2.5 g (5%) methylene-bis-methallylmalonic ester, m.p. 44-45° (upon recrystallization from dilute alcohol).

6.650 mg sub.: 15.235 mg CO_2; 5.000 mg H_2O. 3.770 mg sub.: 8.650 mg CO_2; 2.850 mg H_2O. Found %: C 62.52, 62.61; H 8.41, 8.46. $C_{23}H_{36}O_8$. Calculated %: C62.67; H 8.24.

Methylene bis-methallylmalonicester is not described in the literature.

3. Secondary pentenylmalonic ester. Reaction of piperylene hydrochloride* (0.5 mole) with sodium malonic ester (0.25 mole) took place under the normal conditions for obtaining dialkylmalonic esters. However, the main reaction product proved to be monosubstituted** malonic ester (secondary pentenylmalonic):

B. p. 115-117° (9 mm), n_D^{20} 1.4402, d_4^{20} 0.9919, MR_D 60.61. Calc. 60.46. Yield was 57% of the theoretical.

6.405 mg sub.: 14.920 mg CO_2; 5.160 mg H_2O. 8.620 mg sub.: 20.040 mg CO_2, 6.910 mg H_2O. Found %: C 63.57, 63.44; H 9.01, 8.97. $C_{12}H_{20}O_4$. Calculated %: C 63.13; H 8.80.

Secondary pentenylmalonic ester is not described in the literature.

4. Barbituric acids. The barbituric acids were obtained by reacting methylene-bis-alkenylmalonic esters, and also secondary pentenylmalonic ester, with urea in the presence of sodium ethylate, in the usual way [1].

The constants and the analytical data for the barbiturates obtained are presented in the table.

Barbituric Acids

Name	Formula	M.p.	% yield	N (in %)	
				found	calculated
Methylene-bis-5-allylbarbituric acid	III	267-268° (decomposed)	52.6	15.85 15.90	16.09
Methylene-bis-5-methallylbarbituric acid	IV	298-299 (decomposed)	40.0	14.55 14.48	14.88
5-Secondary-pentenylbarbituric acid	V	147-148	98.0	14.99 14.94	15.20

SUMMARY

1. A study was made of the reactions between methylene-bis-sodium malonic esters and the primary unsaturated chlorides – allyl chlorides and methallyl chloride.

2. It was determined that the alkenylhalides of allyl type behave like the alkylhalides in this reaction: when the primary chloride of normal structure is used – the allyl chloride – the yield of methylene-bis-allylmalonic ester attains 30.6%, while when the primary chloride of branched structure – methallylchloride – is used, the yield of methylene-bis-methallylmalonic ester is only 5% of the theoretical.

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* Piperylene hydrochloride was obtained by saturating piperylene with gaseous hydrogen chloride, with cooling. The hydrochloride thus obtained was reacted without prior distillation.

** Diallyl- and dimethallylmalonic esters were obtained under the same conditions and with the same reagent proportions, in 71 and 55 % of theoretical yield, respectively.

3. It was shown that when allylation of methylene-bis-malonic ester occurs, the same side-reaction takes place as when it is alkylated – there is a cleavage of an intermediate product, monoalkenyl-methylene-bis-malonic ester, under the influence of sodium ethylate, into methylene-malonic ester (which later converts to the crystalline polymer) and monoalkenylmalonic ester; the latter reacts further readily with allyl halides, resulting in the formation of dialkenylmalonic ester. This side reaction occurs to a greater degree when the chloride of branched structure is used, and the yields of diallyl- and dimethallylmalonic esters constitute, respectively, 58 and 87% of the theoretical.

4. The following acids were obtained that are not described in the literature: methylene-bis-5-allylbarbituric, methylene-bis-5-methallylbarbituric and 5-secondary-pentenylbarbituric.

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* T. p. = C. B. Translation pagination.

SYNTHESIS OF ALKOXYETHYLIDENELACTAMS

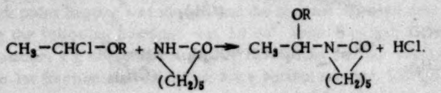
I. ALKOXYETHYLIDENECAPROLACTAMS

M. F. Shostakovsky and F. P. Sidelkovskaya

Alkoxyethylidenelactams are of considerable interest in that they belong to the group of compounds simultaneously containing nitrogen and oxygen with a single carbon atom.

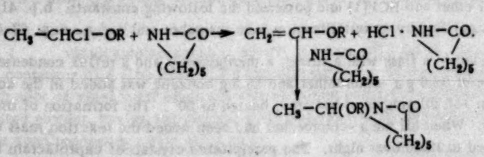
This research resulted in the production and description of alkoxyethylidenecaprolactams. A number of reactions were investigated with their production in mind: reaction of α-chloroethylalkyl ethers with caprolactams, addition of caprolactam to vinylalkyl ethers, and addition of alcohols to vinylcaprolactam.

We obtained our best results by the first method, i.e., by reacting α-chloroethylalkyl ethers with caprolactam. The reaction is exceptionally easy to obtain and proceeds at room temperature. Slight elevation of temperature speeds the process (50-60°) and facilitates improved yield. The reaction was studied in greatest detail when α-chloroethyl butyl ether was used. It is important to state that the yield of products depends heavily on the ratio of the initial materials. With a 1 : 1 ratio the reaction products are caprolactam hydrochloride, butoxyethylidenecaprolactam (24.7 %), butanol and dibutylacetal. The greater the proportion of caprolactam in the reaction, the greater the resulting butoxyethylidenecaprolactam and caprolactam hydrochloride content, and the less the butanol and dibutylacetol. The maximum butoxyethylidenecaprolactam yield (70%) is obtained at a 2 : 1 ratio of caprolactam to α-chloroether. Further increase in the caprolactam content of the reaction mixture leads to no further rise in yield, as it seriously complicates formation of the products and their liberation in pure form. The results obtained led us to the conclusion that the reaction between α-chloroethers and caprolactam proceeds in two stages. The first stage consists of the replacement of the excess caprolactam by the α-halide of halogenated ether (equation 1), and the second, of the combination of the liberated HCl with the initial caprolactam, which explains why twice as much of the latter is required.



$$CH_3-CHCl-OR + \underbrace{NH-CO}_{(CH_2)_5} \rightarrow CH_3-\overset{OR}{CH}-\underbrace{N-CO}_{(CH_2)_5} + HCl. \qquad (1)$$

The high reactive capacity of the α-chloro ethers and their tendency to exchange the α-atom of chlorine for other atoms and groups is well known [1]. In the given instance this process is facilitated by the production of the crystalline hydrochloride, which is insoluble in the reaction mass. The presence of butanol and dibutylacetal in the reaction products may be explained by the partial decomposition of the α-chloro ether not reacted in equation (1). The possibility that a corresponding decomposition of the butoxyethylidenecaprolactam formed in the reaction may also take place must be considered as well. The following reaction mechanism is also possible in addition to that adduced above:



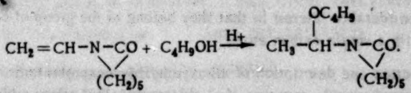
$$CH_3-CHCl-OR + \underbrace{NH-CO}_{(CH_2)_5} \rightarrow CH_2=CH-OR + HCl\cdot\underbrace{NH-CO.}_{(CH_2)_5} \qquad (2)$$

$$CH_2=CH-OR \xrightarrow{\underbrace{NH-CO}_{(CH_2)_5}} CH_3-CH(OR)\underbrace{N-CO}_{(CH_2)_5}$$

In the latter case the initial process is not exchange of the α-atom of chlorine, but splitting of the hydrogen halide. The second stage consists of addition of caprolactam to the vinyl butyl ether. The ability of α-halogenated ethers to split HX under the influence of organic bases has been described in various papers [1,2]. However, the first course seems the more probable to us, as: a) the alkalinity of caprolactam, as an amphoteric compound, cannot be high enough to cause the splitting off of hydrohalic acid; b) vinyl butyl ether was not liberated in a single experiment; and c), as will be seen below, the addition of caprolactam to vinyl butyl ether proceeds with difficulty and leads to a very negligible yield of alkoxyethylidenecaprolactam.

It is well known from the researches of our laboratory [3], that simple vinyl ethers of the $CH_2{=}CH{-}OR$ type readily combine with various substances containing a free hydrogen atom, if acid catalysts are present. This made it possible to postulate the successful combination of caprolactam with vinyl butyl ether. When they were heated in presence of minute quantities of hydrochloric acid we did obtain butyoxyethylidenecaprolactam, the yield, however, was exceedingly small (2.7 %). Butanol and dibutylacetal were obtained as by-products.

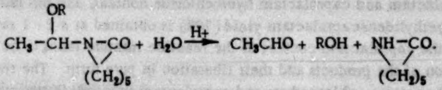
In an effort to extend the methods of synthesizing alkoxyethylidenecaprolactam, and to study the properties of the vinylcaprolactam previously obtained [4], we investigated the reaction caused when alcohols were added to the latter. Heating of vinylcaprolactam with methyl, ethyl and butyl alcohols in presence of an alkaline catalyst (KOH) failed to produce alkoxyethylidenecaprolactam. An approximately 8.5% yield of butoxyethylidenecaprolactam was produced when vinylcaprolactam was reacted with butanol in presence of hydrochloric acid under the conditions prescribed for the synthesis of dialkylacetal [5] (immediate mixture of the components).



$$CH_2{=}CH{-}\underset{\diagdown(CH_2)_5\diagup}{N{-}CO} + C_4H_9OH \xrightarrow{H+} CH_3{-}\overset{OC_4H_9}{CH}{-}\underset{\diagdown(CH_2)_5\diagup}{N{-}CO}. \tag{3}$$

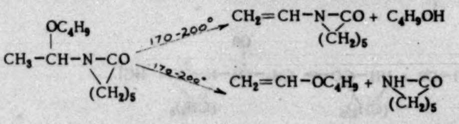
There was no appreciable increase in yield when more severe conditions were applied (elevation of temperature and increased duration of the experiment): the reaction was accompanied by side-reactions (production of resins and disproportionation. However, these experiments demonstrated that the combination of alcohols strated with vinylcaprolactam proceeds in accordance with Markovnikov's law, as does their combination with vinyl alkyl ethers [4].

The ethoxy- and butoxyethylidenecaprolactam synthesized in this research are colorless viscous liquids which decompose upon distillation at atmospheric pressure. They hydrolyze into a dilute acid with the formation of acetaldehyde, caprolactam and the corresponding alcohol, as is confirmed by their structure.



$$CH_3{-}\overset{OR}{CH}{-}\underset{\diagdown(CH_2)_5\diagup}{N{-}CO} + H_2O \xrightarrow{H+} CH_3CHO + ROH + \underset{\diagdown(CH_2)_5\diagup}{NH{-}CO}. \tag{4}$$

Decomposition under heat, carried out with butoxyethylidenecaprolactam, was of considerable interest. Heating of this compund to 170 to 200° gave butanol and vinylcaprolactam (partially as monomer, partially as polymer):



$$CH_3{-}\overset{OC_4H_9}{CH}{-}\underset{\diagdown(CH_2)_5\diagup}{N{-}CO} \xrightarrow{170\text{-}200^\circ} CH_2{=}CH{-}\underset{(CH_2)_5}{N{-}CO} + C_4H_9OH \tag{5}$$

$$CH_3{-}\overset{OC_4H_9}{CH}{-}\underset{\diagdown(CH_2)_5\diagup}{N{-}CO} \xrightarrow{170\text{-}200^\circ} CH_2{=}CH{-}OC_4H_9 + \underset{(CH_2)_5}{NH{-}CO} \tag{6}$$

Simultaneously with this main direction of reaction, decomposition also proceeds to a very limited degree in another manner, i.e., by the splitting of caplolactam and the liberation of inyl butyl ether (equation 6). Reactions 5 and 6 are further examples of indirect vinylation, as worked out by Shostakovsky and his associates [6].

EXPERIMENTAL

1. Reaction of α-chloroethyl butyl ether with caprolactam in 1 : 2 mole ratio. The α-chloroethyl butyl ether was produced from vinyl butyl ether and HCl [1] and possessed the following constants: b.p. 41-42°, 17 mm, n_D^{21} 1.4172. The caprolactam was purified by recrystallization from the ether and had a m.p. 67-68°.

The reaction was conducted in a flask with a stirrer, a thermometer and a reflux condenser, provided with a calcium chloride tube. A mixture of 32.6 g α-chloroether and 55.5 g benzene was added in the course of 2.5 hours to a solution of 70 g caprolactam in 140 ml anhydrous benzene, heated to 50°. The formation of small white crystals was noted within 20 to 30 minutes. When all the α-chloroether had been added the reaction mass was heated at 50° for another three hours and allowed to stand over night. The precipitated crystals of caprolactam hydrochloride were filtered out, washed in anhydrous ether and dried in a vacuum dessicator. The weight of the crystals was 33 g (91.4 %), m.p. 142-143° (from dichloroethane). The hygroscopicity of the crystals made it impossible to obtain a m.p. in a small interval.

Found %: HCl 23.85, 25.14. $C_6H_{12}ONCl$. Calculated %: HCl 24.37.

Neutralization of the hydrochloric caprolactam by a solution of caustic potash produced caprolactam, m.p. 67-68°; a sample mixed with caprolactam of known purity had m.p. 67°.

The benzene and ether filtrates obtained after the caprolactam hydrochloride was separated out, were neutralized with ammonia, the ammonium chloride was filtered out, and the solution washed five times in water, dried with potash and vacuum distilled. This gave 1.1 g dibutylacetal (b.p. 180-185°, n_D^{20} 1.4090), 36.6 g (71.9%) butoxyethylidenecaprolactam (b.p. 116-117°, 2.8 mm), and 1.2 g resin. Salting out and distillation produced 19 g of the initial caprolactam from the washings. The botoxyethylidencaprolactam constants were:

n_D^{20} 1.4645, d_4^{20} 0.9774, MR_D 60.27; calculated 61.01.

Found %: N 6.77, 6.58; C 67.28, 67.54; H 11.04, 10.80, M 200.6, 199. $C_{12}H_{23}O_2N$. Calculated %: N 6.56; C 67.56; H 10.86. M 213.3.

2. Reaction of α-chloro ethyl butyl ether with caprolactam at 1:1 mole ratio. The reaction was produced by the method indicated in Experiment 1. 29.3 g of α-chloroether in 30 ml benzene was added to a solution of 25 g caprolactam in 50 ml benzene. The hydrochloric caprolactam was filtered out, and the filtrate put through the appropriate processes. This gave 2 g butanol (b.p. 115-117°, n_D^{20} 1.3999), 7.3 g dibutylacetal, 10.3 g (24.79%) butoxyethylidenecaprolactam and 7 g resin.

3. Reaction of α-chlorodiethyl ether with caprolactam. 20 g chlorodiethyl ether in 20 ml anhydrous benzene was added to 52 g caprolactam in 110 ml benzene under the conditions of Experiment 1. Crystals of hydrochloric caprolactam, b.p. 142-148°, were precipitated. Processing of the benzene filtrate, as in Experiment 1, gave 15 g (44%) ethoxyethylidenecaprolactam (b.p. 100-101°, 2.6 mm), 13.5 unreacted caprolactam and 1.5 g resin. The constants of the ethoxyethylidenecaprolactam were:

n_D^{20} 1.4806, d_4^{20} 1.0112, MR_D 52.13; calculated 51.77.

Found %: N 7.26, 7.35. $C_{10}H_{19}O_2N$. Calculated %: N 7.56.

4. Addition of caprolactam to vinyl butyl ether. 3 drops (0.05 g) concentrated HCl was added to a mixture of 33 g caprolactam, 29 g vinyl butyl ether and 40 ml dry acetone, heated to 53°; the mixture was boiled for ten minutes and allowed to stand overnight. When the solvent was driven off at 150 mm the following remained: a substance with a b.p. of 20-50° 50 mm and a viscous residue which crystallized rapidly. Distillation of the fraction of b.p. 20-50°, 50 mm, gave 17 g unreacted vinyl butyl ether: the undissolved portion consisted of 21.6 caprolactam, while distillation of the ether solution gave 1.5 g butanol, 1.5 g dibutylacetal and 1.7 g butoxyethylidene aprolactam (2.7%).

5. Addition of butanol to vinylcaprolactam. 2 drops concentrated HCl were added to a mixture of 21.3 g vinylcaprolactam and 17 g butanol, heated to 43°; the temperature rose rapidly to 105°. This temperature was retained for five minutes, at which point heating was stopped and the reaction mass left over night. Neutralization with potash, and distillation gave the following fractions: 1st, 35-95°, 4mm, 8 g; 2nd, 8 g 97-104°, 4 mm; 3rd, 18.2 g, 104-114° 4 mm; 2 g resinous residue; 1 g of product having n_D^{18} 1.4010, in the trap, cooled to −40°. The contents of the trap were merged with the 1st fraction and redistilled; 5.9 g butanol resulted. 13.6g unreacted vinylcaprolactam, 1.8 g resin and 7.1 impure butoxyethylidenecaprolactam, from which 2.8 g (8.5%) of the pure product was obtained, were recovered from the 2nd and 3rd fractions. 0.5 g of a crystalline substance whose structure was not determined was formed in the resinous residue when permitted to stand.

6. Thermal decomposition of butoxyethylidenecaprolactam. 11.2 g butoxyethylidenecaprolactam was heated for two hours at 170-200° in a Favorsky retort, connected in series with a Liebig condenser, a receiver and a coil trap cooled to −40°. Distillation of the reaction mass in vacuum gave the following fractions: 1st, 36-92°, 3.2 mm, 2 g; 2nd, 92-98° 3.2 mm, 2.8 g; 3rd, 98-108°, 3.2 mm, 6.2 g; n_D^{26} 1.4820. Trap contents − 1.5 g; resin 1.9 g.

Redistillation and appropriate cleansing of the separate fractions (washing with water, drying with potash) gave 2g butanol, 1.3 g vinylcaprolactam (b.p. 93-97°, 3.5 mm, n_D^{20} 1.5075). Bisulfite titration [7] established the vinylcaprolactam content − 97.8 (100.9%); 0.2 g caprolactam (m.p. 67-68°); approximately 0.2 g of a fraction with 50-95° b.p. with odor of vinyl butyl ether and demonstrating positive qualitative reactions for vinyl ethers; 0.7 g of a slightly tinted powder, having the characteristic qualities [4] of polyvinylcaprolactam, was recovered from the resinous residue upon processing with ethyl ether.

3.803 mg substance: 14.1 ml 0.02 N $KH(IO_3)_2$. Found %: N 10.34. $(C_8H_{13}ON)_n$. Calculated %: N 10.07.

7. Hydrolysis of butoxyethylidenecaprolactam. 10 g butoxyethylidenecaprolactam and 100 ml 2% H_2SO_4 were heated for 3 hours at 80° in a retort with reflux condenser under constant stirring and ventilation with a nitrogen stream. The reflux condenser was connected with three ice-cooled Tishchenko flasks, each containing 40 ml water. Within 30 minutes the reaction mass became homogenous. When heating was concluded, the reaction product was neutralized with barium carbonate, the $BaSO_4$ was filtered out, and the filtrate distilled. This gave a fraction with

b.p. 92-98°, from which 3.1 g butanol and a resinous residue were obtained. Boiling ether extraction of the resin gave 3.3 g caprolactam with m.p. 67°.

The contents of the Tishchenko flasks gave a residue of 2,4-dinitrophenylhydrazone acetaldehyde (m.p. 159°, from alcohol). Bisulfite titration of an aliquot portion gave 0.9599 g acetaldehyde.

8. Hydrolysis of ethoxyethylidenecaprolactam. 9.8 g ethoxyethylidenecaprolactam was hydrolyzed in presence of sulfuric acid. The reaction procedure and separation of the products followed that in Experiment 7. 2.5 g caprolactam with m.p. 67-68° was recovered. An acetaldehyde derivative, m.p. 157° (from alcohol) was produced by reacting the solutions collected from the Tishchenko absorption flasks with 2,4-dinitrophenylhydrzzine. On bisulfite titration 1.533 g acetaldehyde was found.

SUMMARY

1. Reaction of caprolactam with α-chloroethyl butyl and α-chlorodiethyl ether produced butoxy- and ethoxyethylidenecaprolactams with a yield of up to 70% of the theoretical.

2. It was shown that addition of caprolactam to vinyl butyl ether, and also addition of butanol to vinylcaprolactam with the purpose of synthesizing butoxyethylidenecaprolactam proceeded very slowly and did not result in a satisfactory yield of the product sought.

3. Synthesized alkoxyethylidenecaprolactams hydrolyze in presence of sulfuric acid with the production of alcohol, caprolactam and acetaldehyde.

4. It was shown that vinylcaprolactam and butanol are the major thermal decomposition products of butoxyethylidenecaprolactam.

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REACTION OF SODIUM SALTS OF CARBOXYLIC ACIDS IN MELTS

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Various methods of physical chemical analysis have been applied to the study of a number of double and more complex salt systems in melts. These studies have permitted our native scientists to deduce certain laws of the direction of processes in salt melts. All these researches have been performed with systems consisting of inorganic acid salts. Study of carboxylic acid salts has been completely inadequate in this regard. Only two systems have been described in the literature. Baskov described the potassium acetate – sodium acetate system in 1915 [1], and a description of a second system, sodium acetate – zinc acetate, appeared rather recently [2].

The purpose of the present work was to employ the visual-polythermic method in studying double systems consisting of the sodium salts of carboxylic acids.

In studies of this type, the reaction of the salt to heating is of decisive importance. Only systems whose components do not decompose upon heating may be studied. Among carboxylic acid sodium salts, only sodium acetate and formate have been thoroughly studied in this regard. According to the literature [3], sodium formate does not decompose after heating to 310° for five hours, and decomposes very slowly at 400°. The addition of caustic alkali greatly accelerates decomposition of the formate [4]. Anhydous sodium acetate, which melts at 331°, may be heated to 390° [5], but at higher temperatures it decomposes into soda and acetone [6]. The addition of an alkaline caustic also facilitates decomposition of this acetate. In general, a mixture of carboxylic acid sodium salt and an alkaline caustic produces a hydrocarbon and soda upon calcination [7]. Sodium formate, acetate and propionate melt and solidify upon cooling as do inorganic acid salts, i.e., heating causes them to change directly from the solid crystalline to the amorphous liquid state, while cooling from the melt results in solid crystals. However, according to the findings of certain writers, the melting and solidfication of carboxylic acid salts containing three or more carbon atoms in the radical proceeds differently. Upon fusing sodium stearate, Adami and Aschoff [9] observed a liquid crystalline phase intermediate between the solid crystalline and the liquid amorphous. Vorländer [8] found a liquid crystalline phase in the majority of organic acid salts having three or more carbon atoms in the radical. These salts have, as it were, two melting points: one representing the transition from the solid crystalline to the liquid crystalline phase, and the second, from the liquid crystalline to the liquid amorphous. They found the following approximate melting points for salts that are components of the systems we studied: 250° and 320° for sodium isobutyrate, 210 and 310° for sodium butyrate, 168 and 260° for sodium isovalerate, 225 and 350 for sodium caproate, 220 and 305° for sodium stearate, and 410 and 430 for sodium benzoate. Vorländer obtained his salts by mixing equivalent quantities either of base and acid (in the presence of a trace of phenolphthalein), or of alcoholate and acid. Acid, base and alcoholate were all used in alcoholic solutions. Neutralization of the base by the acid caused concentration of the salt solution, and when the alcoholate was used the salt was displaced from the alcohol by ether. In our opinion, the difficulty of determining the equivalent point under these conditions, and also the use of equivalent quantities of substances to obtain the salts, create the possibility that salt obtained in this way may be contaminated by alkali or acid. Therefore we obtained our salts by reacting an excess – always – of acid with an aqueous soda solution; the aqueous salt solution was concentrated, and the salt was then dried to complete elimination of excess acid.

Slow cooling of transparent melts of these salts in test tubes accompanied by constant stirring with a fine glass stirrer resulted first in clouding, and then in the formation of a pasty mass which solidified during a specific temperature interval. Sodium formate, acetate and isobutyrate separated out as crystals upon cooling from melts, as do inorganic acid salts. We took as the melting point (the point at which the first crystals appeared) for both pure salt and salt mixtures the temperature at which the homogeneity of the melt disappeared. In some cases this corresponded to the appearance of clouding, and in others to the appearance of crystals.

EXPERIMENTAL

For optimum uniformity of heating, the test tube containing the salts was placed in a larger test tube. A glass filament (mixer) was placed in the test tube containing the salts, and the hot point of a nichrome-constantan thermocouple was placed in the glass jacket; the other point was placed in a Dewar flask at a specific temperature. The thermocouple was connected to a mirror-scale galvanometer at 17 millivolts.

To translate the millivoltmeter scale information into degrees of temperature, a datum point curve was plotted on the basis of the following melting points: benzoic acid 122.5°, mannitol 166°, tin 232°, cadmium 321°, potassium nitrate 337°, potassium bichromate 397.5°, zinc 419.5°, lead chloride 498°, and the boiling point of sulfur, 444.6°. Based on this datum point curve the melting points (the temperature of onset of crystallization) of the components were: sodium formate 258°, sodium acetate 331°, sodium butytate 330°, sodium isobutyrate 260°, sodium isovalerate 262°, sodium caproate 365°, sodium stearate 308°, and sodium benzoate 463°.

Commercial sodium acetate, sodium stearate and sodium benzoate were used. The remaining salts were synthesized by us, starting with sodium carbonate solution and the particular acid. The sodium carbonate and acid were first purified by distillation. To produce the salt, the acid was added, bit by bit, with constant stirring, to the aqueous sodium carbonate solution (cold when the formate was desired, and hot for synthesis of the remaining salts) first until a neutral reaction was obtained; a one or two ml excess of acid was then added, until litmus paper gave a clearly acid reaction. The salt solution was evaporated to dryness in a porcelain cup over a water bath. The dry residue was carefully pulverized and dried in a desiccator at 160° until the acid odor disappeared completely. When acid (acid salt) admixture was missing, the salt solution showed a clearly basic reaction on litmus paper, and, in the second place, the same sample of salt showed no change in melting point upon several consecutive melts. A salt with acid impurity, or acid salt showed an increased melting point at each new melt, and drops of water would appear on the sides of the test tube as a result of liberation of acid or decomposition of the acid salt. When salt is obtained in this manner it is absolutely essential to use excess acid. If a salt solution obtained by mixing equivalent portions of soda and acid be evaporated, the dry residue will darken when heated in a desiccator, and when subjected to melting will decompose before reaching the melting point. When this occurs the decomposition of the salt is most probably due to an admixture of alkali. Evaporation results in partial hydrolysis of the salt, and the acid formed is volatilized with the water vapor, while the alkali remains to contaminate the salt. Removal of the excess acid during synthesis of sodium formate, isobutyrate, butyrate and caproate presented no difficulty. Elimination of the excess acid proved more difficult during isovalerate synthesis due to the tendency of this compound to produce stable acid salts. In this instance the residue after drying was carefully melted, without overheating, poured over a hot plate in a thin layer, and pulverized while hot.

Desiring to trace the effect of the salt hydrocarbon radical upon the processes of fusion, we divided the systems investigated into seven groups. In each of these groups, one component was identical for all systems.

The systems containing sodium benzoate were not studied fully, but only to a given sodium benzoate content, as further addition of this compound led to a rise in the temperature of fusion of the mixture, and to its decomposition. It was not possible to add other salts to the benzoate because of its high melting point (463°), at which other salts decompose.

All compositions are given in molecular percentages.

1. Systems with sodium formate.

The fusibility curve of the sodium formate-sodium acetate system (Fig. 1), Table consisted of two branches, intersecting at a eutectic point reached at 242° and 10.5% acetate.

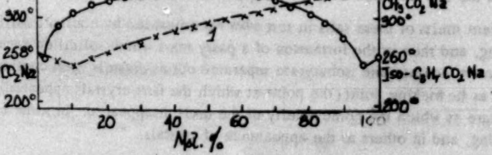

Fig. 1. Fusibility curves of systems:

1) Sodium formate–sodium acetate; 2) sodium formate–sodium isobutyrate.

Three branches of the crystallization curve in the sodium formate-sodium butyrate system (Fig. 2, Table 1) intersect at two eutectic points: 252° and 2.5% butyrate, and 318° and 89% butyrate. A compound that fused without decomposition was formed: $HCOONa \cdot C_3H_7COONa$. The fusibility curve of the sodium formate–sodium isobutyrate system (Fig. 1, Table 1) consist of three segments intersecting at two eutectic points: 252° and 1.3% isobutyrate, and 250° and 96.5% isobutyrate. A compound was formed that fused without decomposition: $HCOONa \cdot iso\text{-}C_3H_7COONa$. The sodium formate – sodium isovalerate system has three curves of crystallization, intersecting at two eutectic points: at 252° and 0.75% isovalerate, and at 245° and 94.5% isovalerate. The following compounds, which fuse without decomposition, were formed $3HCOONa \cdot 2\ iso\text{-}C_4H_9COONa$ (Fig. 2, Table 1).

TABLE 1

Acetate (%)	Onset of crystallization	Butyrate (%)	Onset of crystallization	Isobutyrate (%)	Onset of crystallization	Isovalerate (%)	Onset of crystallization
0	258°	0	258°	0	258°	0	258°
5	252	2.5	252	1.3	252	0.75	252
10	244	5	287	5	290	5	287
10.5	242	10	301	10	305	10	300
15	252	15	312	15	314	15	308
20	260	20	318	20	319	20	311
25	267	25	324	25	321	25	314
30	270	30	327	30	324	30	316
35	278	35	333	35	326	35	318
40	284	40	337	40	327	40	320
45	291	45	339	45	329	45	319
50	296	50	341	50	330	50	317
55	300	55	340	55	329	55	315
60	303	60	340	60	327	60	312
65	308	65	339	65	325	65	309
70	313	70	338	70	320	70	306
75	316	75	336	75	314	75	301
80	320	80	331	80	306	80	297
85	323	85	324	85	296	85	284
90	326	89	308	90	282	90	265
95	330	90	311	95	258	94.5	245
100	331	95	322	96.5	250	100	262
		100	330	100	260		

Sodium caproate proved to be negligibly soluble in the fused formate in a sodium formate-sodium caproate system. Sodium formate decomposed upon being added to fused sodium caproate.

In the sodium formate-sodium stearate system, the components would not mix when fused.

In the sodium formate-sodium benzoate system, the latter was not soluble in the former when fused. Upon heating to the melting point of the benzoate, the formate decomposed.

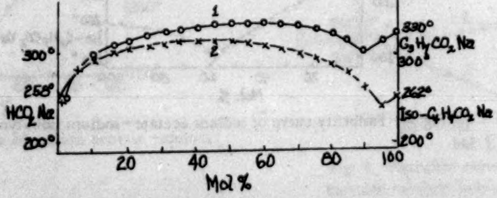

Fig. 2. Fusibility curves of systems:
1) Sodium formate–sodium n-butyrate; 2) sodium formate–sodium isovalerate.

The data obtained by study of the systems comprising sodium formate (Table 1) show that: 1) sodium acetate, butyrate, isobutyrate and isovalerate, when fused, were miscible with sodium formate; the caproate and stearate were not miscible. It is possible that other fatty acid salts containing more than five carbon atoms in the radical may not be miscible in melts with formate. Neither did sodium benzoate mix with the formate in a melt. 2) An increase in the number of carbon atoms in the radical of a fatty acid salt facilitates complex formation. Sodium acetate and butyrate, having very similar melting points (331 and 300°) reacted differently with the formate. Complex formation did not occur in the sodium formate-sodium acetate system, but it did with the others. 3) Branching of the carbon chain without variation in the number of carbon atoms in the radical does not affect the nature of the reaction between salts and sodium formate; complex formation was noted in systems embracing the butyrate and the isobutyrate. 4) A rise in the number of carbon atoms in the radical of the second component in these systems brings a reduction in the primary crystallization of the formate side. Thus, in the system formed with the acetate, the share of the formate was 10.5%, with butyrate it was 2.5%, and with isovalerate it was only 0.75%.

2. Sodium acetate systems.

The three curves of crystallization (Fig. 3, Table 2) in the sodium acetate-sodium butyrate system are intersected at two eutectic points, 266° and 33.5% butyrate, and 250° and 69% sodium butyrate. The compound formed was $3CH_3COONa \cdot 2C_3H_7COONa$.

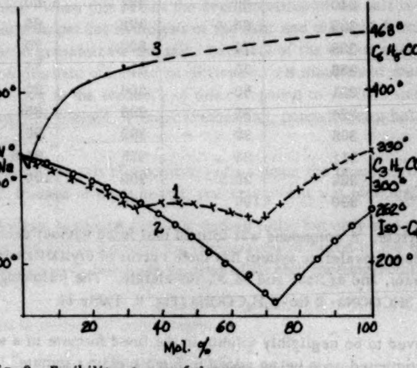

Fig. 3. Fusibility curve of the system.
1) Sodium acetate and sodium butyrate; 2) sodium acetate and sodium isovalerate; 3) sodium acetate and sodium benzoate.

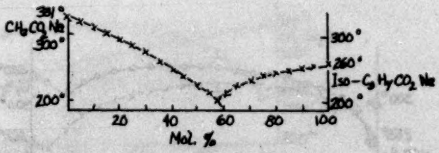

Fig. 4. Fusibility curve of sodium acetate—sodium isobutyrate.

TABLE 2

Butyrate, (%)	Onset of crystallization	Isobutyrate, (%)	Onset of crystallization	Isovalerate, (%)	Onset of crystallization	Caproate, (%)	Onset of crystallization	Benzoate, (%)	Onset of crystallization
0	331°	0	331°	0	331°	0	331°	0	331°
5	319	5	323	5	320	5	321	2.6	315
10	309	10	314	10	311	10	312	5	350
15	299	15	305	15	304	15	304	10	380
20	290	20	297	20	295	20	296	15	400
25	282	25	288	25	287	25	288	20	411
30	274	30	277	30	280	30	279	25	421
33.5	266	35	265	35	269	34.5	268	30	428
35	268	40	254	40	260	35	269	33	431
40	273	45	242	45	248	40	269	100	465
45	270	50	230	50	232	45	265		
50	268	55	218	55	215	49.5	260		
55	265	58	208	60	199	50	265		
60	260	60	215	65	184	55	300		
65	254	65	226	70	166	60	321		
69	250	70	236	73	156	65	332		
70	253	75	242	75	163	70	342		
75	266	80	246	80	185	75	349		
80	281	85	250	85	207	80	353		
90	312	90	254	90	228	90	360		
95	324	95	257	95	247	95	363		
100	330	100	260	100	262	100	365		

The sodium acetate-sodium isobutyrate system fusibility curve shows two branches (Fig. 4, Table 2) intersected at a eutectic point, 208° and 58% sodium isobutyrate.

The two branches of the fusibility curve of the sodium acetate-sodium isovalerate system are intersected at a eutectic point at 156° and 73% sodium isovalerate.

The three branches of the fusibility curve of the sodium acetate-sodium caproate system (Fig. 5, Table 2) are intersected at two eutectic points at 268° and 34.5% sodium caproate, and 260° and 49.5% sodium caproate. The compound formed was $5CH_3COONa \cdot 3C_5H_{11}COONa$.

The sodium acetate-sodium benzoate system, studied only up to 33% benzoate content, shows two branches of crystallization (Fig. 3, Table 2), intersecting at a eutectic point at 315° and 2.6% sodium benzoate.

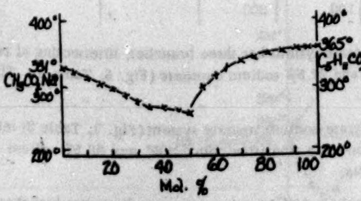

Fig. 5. Fusibility curve of sodium acetate—sodium caproate system.

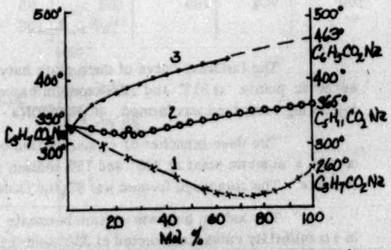

Fig. 6. Fusibility curves of systems: 1) Sodium butyrate—sodium isobutyrate; 2) sodium n-butyrate—sodium caproate; 3) sodium n-butyrate—sodium benzoate.

In a sodium acetate-sodium stearate system, these compounds failed to mix in the fused state.

The research data for systems formed with sodium acetate show that: (1) sodium formate, butyrate, isobutyrate, isovalerate, caproate and benzoate are miscible with sodium acetate in melts. Sodium stearate is not miscible. (2) Complex formation is observed in systems whose second component is the salt of a fatty acid with unbranched carbon atom chain in the radical. Thus, sodium butyrate and caproate combine with sodium acetate to produce: $3CH_3COONa \cdot 2C_3H_7COONa$ and $5CH_3COONa \cdot 3C_5H_{11}COONa$. (3) Complex formation does not take place in the systems whose second component is the salt of a fatty acid with a branched carbon atom chain in the radical; sodium isobutyrate and isovalerate do not form compounds with sodium acetate. Sodium acetate decomposed spontaneously when heated above 390°, while in a system with the benzoate it resisted decomposition up to 430°.

3. Systems with sodium butyrate.

The sodium butyrate-sodium isobutyrate system formed an uninterrupted series of solid solutions from a minimum at 221° and 72.5% sodium isobutyrate (Fig. 6, Table 3).

The two branches of the fusibility curve in the sodium butyrate-sodium isovalerate system (Fig. 7, Table 3) intersected at a eutectic point at 257° and 90.5% sodium isovalerate.

TABLE 3

Isobutyrate, (%)	Onset of crystallization	Isovalerate, (%)	Onset of crystallization	Caproate, (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Benzoate, (%)	Onset of crystallization
0	330°	0	330°	0	330°	0	330°	0	330°
5	317	5	326	5	328	5	289	0.13	330
10	306	10	323	10	324	10	261	5	349
15	297	15	320	15	320	15	248	10	361
20	287	20	316	20	318	20	277	15	370
25	279	25	312	22.5	317	25	317	20	378
30	270	30	308	25	321	30	351	25	386
35	264	35	305	27.5	317	35	379	30	394
40	257	40	300	30	319	40	390	35	401
45	250	45	295	35	323	45	389	40	408
50	242	50	292	40	326	50	386	45	415
55	235	55	287	45	331	55	380	50	421
60	229	60	284	50	334	60	376	55	427
65	224	65	281	55	340	65	370	60	434
70	222	70	277	60	343	70	364	100	463
72.5	221	75	273	65	344	75	358		
75	222	80	269	70	349	80	350		
80	225	85	263	75	353	85	340		
85	228	90	258	80	356	90	330		
90	235	90.5	257	85	359	95	314		
95	248	95	263	90	360	96.5	309		
100	260	100	262	95	363	98.5	312		
				100	365	100	308		

The fusibility curve of the sodium butyrate-sodium caproate system has three branches, intersecting at two eutectic points: at 317° and 22.5% sodium caproate and at 317° and 27.5% sodium caproate (Fig. 6, Table 3). The following compound was formed: $4C_3H_7COONa \cdot C_5H_{11}COONa$.

The three branches of crystallization of the sodium butyrate-sodium stearate system (Fig. 7, Table 3) intersect at a eutectic point at 248° and 15% sodium stearate , and at a transition point, 309° and 96.5% sodium stearate. The compound formed was $3C_3H_7COONa \cdot 2C_{17}H_{35}COONa$.

The sodium butyrate-sodium benzoate system, studied only to 60% benzoate content, shows two branches in its fusibility curve, intersected at 330° and 0.13% sodium benzoate.

The results of the studies of systems with sodium butyrate show that: (1) all the fatty acid salts we studied, and sodium benzoate, were miscible with sodium butyrate; (2) complex formation occurred in systems where the second component was a fatty acid salt whose radical contained a straight carbon chain; (3) complex formation did not occur in systems whose second component was a fatty acid salt whose radical contained a side chain.

In the sodium isobutyrate-sodium benzoate system, studied only to 80% sodium benzoate content, the fusibility curve (Fig. 9, Table 4) has two branches, which intersect at a eutectic point at 228° and 3.5% sodium benzoate.

Comparison of the data of systems containing sodium isobutyrate shows that: (1) all the salts studied were miscible in melts with sodium isobutyrate; (2) sodium isobutyrate, whose radical contains a branched carbon atom chain, formed complexes with the formate and the stearate; (3) an uninterrupted series of solid solutions was formed between sodium isobutyrate and sodium butyrate, from whih it differs in melting point and structure of radical, but with which it is identical in the number of carbon atoms in the radical; (4) the isobutyrate also formed an uninterrupted series of solid solutions with sodium isovalerate. These two salts have similar melting points and radicals of analogous structure.

5. Systems with sodium isovalerate.

The sodium isovalerate-sodium caproate system formed an uninterrupted series of solid solutions with a minimum at 239° and 20% sodium caproate (Fig. 10, Table 5).

The three branches of primary cyrstallization in the sodium isovalerate-sodium stearate system are intersected at two points: the eutectic at 140° and 17.3% sodium stearate, and the transitional, at 309° and 92% sodium stearate. The compound formed was iso-$C_4H_9COONa \cdot 2C_{17}H_{35}COONa$.

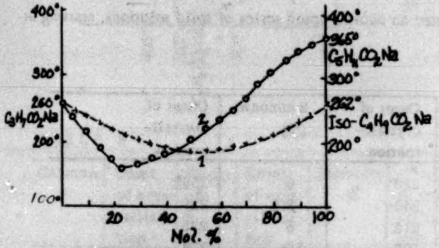

Fig. 8. Fusibility curve of the system:
1) Sodium isobutyrate – sodium isovalerate.
2) sodium isobutyrate – sodium caproate.

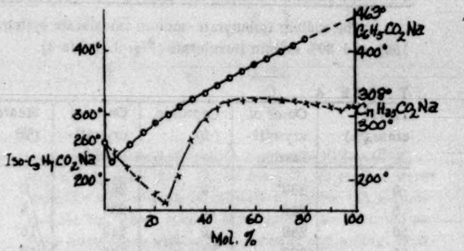

Fig. 9. Fusibility curve of the system:
1) Sodium isobutyrate – sodium stearate.
2) sodium isobutyrate – sodium benzoate.

The sodium isovalerate-sodium benzoate system was studied up to 70% sodium benzoate content. The fusibility curve has two branches, intersecting at 261° and 3% sodium benzoate (Fig. 10, Table 5).

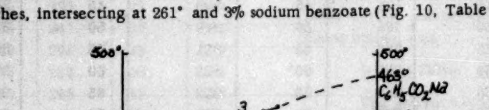

Fig. 10. Fusibility curves of systems:
1) Sodium isovalerate – sodium caproate; 2) sodium isovalerate – sodium stearate; 3) sodium isovalerate – sodium benzoate.

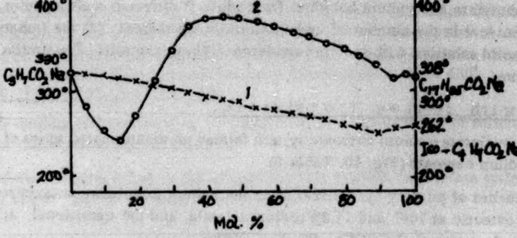

Fig . 7. Fusibility curves of systems;
1) Sodium butyrate—sodium isovalerate;
2) Sodium butyrate, sodium stearate.

4. Systems with sodium isobutyrate

The sodium isobutyrate-sodium isovalerate system formed an uninterrupted series of solid solutions, starting at 189° and 50% sodium isovalerate (Fig. 8, Table 4).

TABLE 4

Isovalerate,(%)	Onset of crystallization	Caproate, (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Benzoate, (%)	Onset of crystallization
0	260°	0	260°	0	260°	0	260°
5	248	5	237	5	240	3.5	228
10	238	10	218	10	215	5	235
15	229	15	195	15	196	10	256
20	220	20	175	20	177	15	272
25	213	23.5	160	25	163	20	288
30	207	25	161	25.5	162	25	301
35	201	30	168	30	217	30	312
40	197	35	175	35	260	35	322
45	193	40	182	40	291	40	335
50	188	45	191	45	309	45	344
55	189	50	205	50	319	50	355
60	191	55	220	55	321	55	367
65	194	60	235	60	323	60	379
70	199	65	252	65	322	65	389
75	207	70	270	70	321	70	399
80	215	75	290	75	320	75	408
85	225	85	329	85	317	100	463
90	237	90	345	90	314		
95	248	95	356	94.5	311		
100	262	100	365	97.5	312		
				100	308		

The two branches of primary crystallization in the sodium isobutyrate-sodium caproate system (Fig. 8, Table 4) are intersected at 160°. and 23.5% by sodium caproate.

The three branches of crystallization in the sodium isobutyrate-sodium stearate system (Fig. 9, Table 4) are intersected at a eutectic point at 162° and 25.5% sodium stearate, and at a transition point at 312° and 97.5% sodium stearate. The compound formed was 2-iso-$C_3H_7COONa \cdot 3C_{17}H_{35}COONa$.

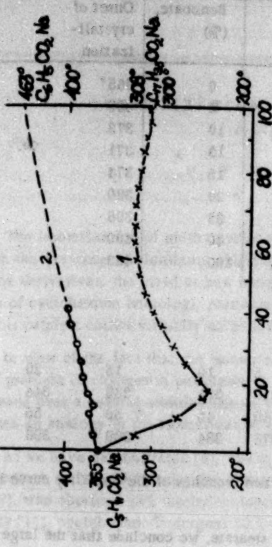

Fig. 11. Fusibility curves of systems: 1- sodium caproate–sodium stearate; 2- sodium caproate–sodium benzoate.

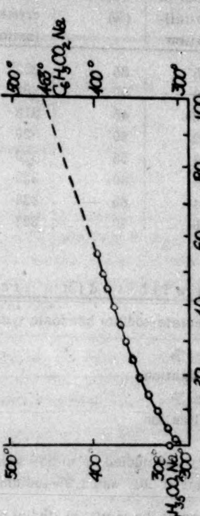

Fig. 12. Fusibility curve of sodium stearate–sodium benzoate system.

TABLE 5

Caproate %	Onset of crystallization	Stearate %	Onset of crystallization	Benzoate %	Onset of crystallization
0	262°	0	262°	0	262°
5	255	5	201	3	261
10	247	10	167	5	275
15	243	15	147	10	298
20	239	17.3	140	15	317
25	242	20	162	20	337
30	248	30	225	25	349
35	256	35	247	30	365
40	263	40	266	35	379
45	271	45	282	40	389
50	277	50	295	45	396
55	283	55	305	50	401
60	291	60	315	55	407
65	296	65	322	60	415
70	304	70	323	65	421
75	313	75	321	70	426
80	322	85	318	100	463
85	331	90	314		
90	341	93.5	309		
95	354	95	312		
100	365	100	308		

The results of studies of systems with sodium isovalerate show that: (1) all the salts we studied were miscible with sodium isovalerate in melts; (2) sodium isovalerate, whose radical has a split chain, reacted to form compounds with sodium formate and sodium stearate, but did not combine with the remaining salts.

6. Systems with sodium caproate.

The three branches of primary crystallization of the sodium caproate–sodium stearate system (Fig. 11, Table 6) are intersected at two points: the eutectic at 239° and 17.5% sodium stearate, and the transitional at 314° and 94.5% sodium stearate. The compound formed was:

$$2C_5H_{11}COONa \cdot 3C_{17}H_{35}COONa$$

The sodium caproate–sodium benzoate system, studied to 40% sodium benzoate content, has two branches in its fusibility curve, intersected at a transition point of 371° and 13% sodium benzoate.

Comparison of the data for the systems with sodium caproate show that: (1) fused sodium caproate reacted with all the salts under study, except sodium formate; (2) complexes were formed in systems whose second component was a salt with a radical of normal structure; and (3) complexes were not formed in systems whose second component contained a radical with branched chain.

TABLE 6

Stearate (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Benzoate, (%)	Onset of crystallization
0	365°	35	293°	75	326°	0	365°
5	320	40	305	80	324	5	369
10	272	45	313	85	321	10	373
15	242	50	320	90	319	13	371
17.5	239	55	326	94.5	314	15	374
20	248	60	329	95	316	20	380
25	264	65	328	100	308	35	396
30	280	70	327			40	400
						100	463

7. System with sodium stearate

Sodium stearate-sodium benzoate system

Sodium benzoate, %	0	1.3	5	10	15	20	24
Onset of crystallization	308°	301	310	321	332	344	353
Sodium benzoate, %	30	35	40	45	50	55	100
Onset of crystallization	362°	369	376	384	390	396	463

The system was studied up to 55% sodium benzoate content. The two branches of the fusibility curve intersect at a eutectic point at 301° and 1.3% sodium benzoate (Fig. 12).

Examination of the results of studies of systems containing sodium stearate, we conclude that the large difference in radical size facilitates complex formation. Thus, the stearate combined with all the fatty acid salts with which it was miscible in melts. This conclusion is confirmed in systems with the formate, as there, too, complexes were formed where there were large differences in radical dimensions. When the difference between radical dimensions was large, the radical structure did not have an important effect upon the character of the reaction. Thus, the formate-butyrate, formate-isobutyrate formate-isovalerate systems resembled each other very closely. This was also true in the stearate systems, whose fusibility curves also show mutual similarity.

Complex formation does not take place, in all probability, in systems containing sodium benzoate.

SUMMARY

28 binary systems formed by carboxylic acid sodium salts were studied. Certain laws were established relative to the effect of the structure of the paraffin portion of carbon acid salt molecules upon processes occurring in salt melts.

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ISOMERIZATION OF METHYLCYCLOHEXANE OVER AN ALUMINOSILICATE CATALYST

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The isomerization of methylcyclohexane has been studied by a number of researchers [1-3], who established that in the presence of aluminum chloride it undergoes isomerization with a narrowing of the ring in the cycloheptane derivatives, the yield at best being 6.3% [4]. Later, Zelinksy and Turova-Polyak [5], studying the isomerization of cyclohexane homologs, particularly methylcyclohexane, in the presence of aluminum chloride, concluded that this catalyst causes virtually no noticeable change in methylcyclohexane.

In view of the fact that the isomerization of naphthene hydrocarbons encountered in petroleum is closely related to the problem of changes in petroleum in nature, it appeared to be of interest to study the isomerization of methylcyclohexane over a natural aluminosilicate catalyst at a temperature not over 250°, particularly as certain researchers [6,7] see an analogy in the isomerization effect of aluminum chloride and of natural aluminosilicate catalysts.

As we have demonstrated [8], this is true of cyclohexane, which undergoes 37 to 40% isomerization to methylcyclopentane at 245-250° under the influence of activated gumbrin, confirming the findings of Nenitzescu and Cantuniari [9], who obtained 22% methylcyclopentane by isomerizing cyclohexane over aluminum chloride. According to Zelinsky [10], cyclohexane undergoes 23.5-24% isomerization to methylcyclopentane in the presence of aluminum chloride.

The methylcyclohexane used in our studies possessed the following constants: b.p. 100.5° (756 mm), d_4^{20} 0.7685, n_D^{20} 1.4235 and contained 0.46% aromatic hydrocarbons (by the aniline method). Equal weights of methylcyclohexane and hydrochloric acid-activated gumbrin (a clay of the montmorillonite type) were placed in a 500 ml high-pressure autoclave and heated by an electric furnace to 245-250°. The duration of heating in various experiments was 50, 70, 90 and 110 hours. Maximum pressure during the experiments did not exceed 25 atm, and fell to zero after cooling of the autoclave. No gas formation was observed in any experiment. At the conclusion of the experiment the product had blended with the catalyst. The product bound by the catalyst was blown out with hot air, freed of water and combined with the general mass. Specific gravity and refractive index were determined after filtration and drying, in order to establish the depth of isomerization of methylcyclohexane (Table 1).

The isomerization products of the first three experiments were distilled in a 100-cm-high Vigreaux fractionating column, five fractions being obtained:) 1st, to 85°; 2nd, 85-90°; 3rd, 90-95°; 4th, 95-100°; 5th, 100-103°.

The first fractions of three experiments, boiling at 44 to 85°, were combined (5.8 g) and distilled in a column with an efficiency of 25 theoretical plates, at the following intervals:

Fraction No.	Boiling point	Weight of fraction (g)	n_D^{20}
1	36-44°	0.39	1.3560
2	44-58	0.06	1.3708
3	58-65	0.59	1.3790
4	65-70	0.92	1.3910
5	70-78	0.95	1.4060
6	78-82	0.48	1.4095
	Residue	1.31	-
	Losses	1.10	-

The fraction boiling at 36-44° corresponded to n-pentane (b.p. 36.8°, n_D^{20} 1.3577) according to its refractive index. The fraction ghat boiled off at 58-65° contained 3-methylpentane (b.p. 63.2°, n_D^{20} 1.3765). The 65-70° fraction corresponded, judging by its refractive index, to a mixture of n-hexane (b.p. 68.8°, n_D^{20} 1.3750) and methylcyclopentane (b.p. 71.9°, n_D^{20} 1.4099). The 70-78° fraction apparently consisted primarily of methylcyclopentane.

The second (85-90°) and third (90-95°) fractions of the catalyzate in the three experiments were combined (63.1 g) and distilled in the same column. Quadruple distillation resulted in the isolation of 24.5 g of a product that boiled

TABLE 1

Heating time (hours)	Methyl-cyclo-hexane charge (g)	Yield of product, %	Constants of the reaction products		Aromatic hydrocarbons, %
			d_4^{20}	n_D^{20}	
50	120	90.83	0.7610	1.4199	0.70
70	120	90.19	0.7600	1.4186	1.11
90	120	89.60	0.7588	1.4180	–
110	120	91.40	0.7585	1.4185	0.78

between 90.1-90.5° and had the following constants: d_4^{20}0.7466, n_D^{20} 1.4105. According to its constants this fraction lay between 1,3-dimethylcyclopentane (d_4^{20} 0.7456, n_D^{20} 1.4092) and trans-1,2-dimethylcyclopentane (d_4^{20} 0.7519, n_D^{20} 1.4117). The composition of this fraction was studied by the Raman spectrum method.

The spectrum of this fraction is given below, together with those of 1,3-dimethylcyclopentane and trans-1,2-dimethylcyclopentane (as given by Bazhulin [11].

Spectrum of 1,3-dimethylcyclopentane	Spectrum of 90.1-90.5° fraction	Spectrum of trans-1,2-dimethylcyclopentane
213 (0), 272 (0),	500 (3), 517 (2),	251(3,w), 262 (6,w),
358 (0), 373 (3,w),	771 (4), 806 (3),	278 (0,w), 326 (0),
419 (0), 426 (3,w),	827 (4), 896 (5),	394 (0), 497 (35),
514 (13), 549 (3),	956 (2), 985 (3),	527 (5), 586 (0), 607 (4,w),
591 (3, dl.) 726 (0),	1081 (1), 1149 (3),	721 (0), 766 (27, dl.),
803 (13,6), 828 (28),	1187 (2), 1316 (2),	798 (0), 861 (5),
878 (0), 950 (3),	1346 (1), 1457 (10),	896 (34), 957 (5,w),
985 (8), 1021 (3,w),	2736 (0), 2865 (8),	1005 (4), 1022 (5),
1041 (3,w), 1085 (3),	2923 (8), 2950 (7).	1081(13, w), 1147 (10),
1100 (3), 1140 (11),		1186 (3,w) 1286 (2),
1152 (11), 1188 (2,w),		1303 (2), 1340(5),
1250 (0), 1298 (2,w),		1360 (3), 1457 (40,w,dl.),
1314 (8), 1346 (5,dl),		2676 (0), 2726 (4),
1457 (40,w), 2725 (4),		2854 (170,w), 2868 (190),
2847 (100,w), (2867), (220),		2906 (100), 2924 (150),
2905 (101),		2957 (230, dl.).
1925 (220), 2953 (220).		

The brightness of the lines was determined visually on a ten-point scale. The degrees of brightness given by Bazhulin were determined with the aid of a microphotometer, so that it was not possible to observe most of the faint lines on the spectrogram obtained. Comparison of the spectra makes clear that the spectrum of the fraction under study contains the lines typical of 1,3-dimethylcyclopentane and trans-1,2-dimethylcyclopentane.

Technical difficulties made it impossible to obtain Raman spectra of the 4th and 5th fractions (95-100 and 100-105°), so that characterization of their composition was limited to determination of boiling point and refractive index. Judging by the refractive index, the fourth fraction (95-100°, n_D^{20} 1.4190) consisted chiefly of a mixture of trans-1,2- and cis-1,2-dimethylcyclopentanes (b.p. 91.9°, n_D^{20} 1.4120 and b.p. 99.2°, n_D^{20} 1.4276, respectively). The constants of the 5th fraction made it possible to postulate that it (b.p. 103.4°, d_4^{20} 0.7669, n_D^{20} 1.4220) consists of an equilibrium mixture of ethylcyclopentane (b.p. 103.4°, d_4^{20} 0.7669 n_D^{20} 1.4197) and methylcyclohexane (b.p. 100.8°, d_4^{20} 0.7692, n_D^{20} 1.4230).

The residue of the first distillations was distilled from a flask with a 20-cm high column. The product distilled in the range of 103-240° (n_D^{20} 1.4426) and contained 6.6% of aromatic hydrocarbons. After they were removed, the product distilled in the range 120-240°, the refractive index was reduced somewhat (n_D^{20} 1.4410), and the specific gravity was d_4^{20}0.8038. Elementary analysis proved the naphthenic character of the hydrocarbons of this fraction.

0.1022 g. sub.: 0.3199 g CO_2; 0.1312 g H_2O. Found %: C 85.32; H 14.28, 0.1133, 0.1615 g sub.; 13.95 g C_6H_6: Δt 0.297°, 0.422°. Found: M 140, 143.

The boiling point, specific gravity and refractive index made it possible to postulate the presence in this fraction of methylated or ethylated homologs of cyclohexane.

To determine the yield of the separate components of the reaction, the catalyzate of the fourth experiment was distilled in a column of 25 theoretical plates, Quadruple distillation yielded the fractions given in Table 2.

TABLE 2

Boiling point	Yield of fraction, (g)	n_D^{20}
37-87°	2.26	1.3925
87-93	11.44	1.4110
93-96	1.47	1.4140
96-100	6.19	1.4187
100-103	16.63	1.4220
103-240	6.97	1.4440
Losses	5.98	–

Table 2 shows that the bulk of the isomerization product of methylcyclohexane fell to fractions corresponding to 1,3-, trans- and cis-1,2-dimethyl cyclopentane (2nd and 4th fractions) and ethyl cyclopentane (5th fraction). A smaller quantity fell to the 6th fractions, containing methylated or ethylated derivatives of cyclohexane, and to the first (methane hydrocarbons).

SUMMARY

The isomerization of methylcyclohexane by a natural aluminosilicate catalyst (gumbrin) at 245-250°, was studied. It was shown that under these circumstances, methylcyclohexane undergoes isomerization, by ring contraction, to cyclopentane derivatives. Methane, aromatic and higher methylated or ethylated cyclohexane homologs are produced in smaller quantities.

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ON THE MECHANISM OF INHIBITOR ACTION

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Kashtanov and Ryzhov [1] have studied the inhibitory action of phenol on the process of oxidation of sulfur dioxide in aqueous solution. Reiter's researches had established [2] that insignificant additions of sulfur dioxide to phenol sharply inhibit the oxidation of the latter by atmospheric oxygen. Thus, there is an interrelation between the inhibitory action of phenol on the process of oxidation of sulfur dioxide and of sulfur dioxide on the autooxidation of phenol by atmospheric oxygen. Phenol is a good inhibitor of the oxidation of tin sulfate [3], chloroform [4] and rubber [5].

TABLE 1

Time (minutes)	Percent oxidation of sodium sulfite		
	Pure	In the presence of agerite	In the presence of neozone
5	9.21	3.75	11.25
15	35.52	8.75	28.75
25	84.21	11.25	57.5
35	97.36	16.25	78.75
45	100.00	22.5	96.25
55	–	27.5	97.5
65	–	27.5	100

In this connection it appeared of interest to determine the action of the rubber oxidation inhibitors now in use, neozone and agerite, upon the rate of oxidation of sodium sulfite.

In these experiments, all inhibitors were used in the form of 0.1% solutions.

Table 1 presents comparative data obtained as described by Kashtanov and Ryzhov [1], on the rate of oxidation of sodium sulfite by atmospheric oxygen in presence of neozone and agerite. These data show that both inhibitors seriously affect the oxidation of sodium sulfite.

Aniline and other amines are used as stabilizers for rubber [7]. Aniline is also a good inhibitor when divalent tin and divalent iron [6] are oxidized by benzaldehyde [8].

TABLE 2

Time (minutes)	Percentage oxidation of sodium sulfite				
	Pure	In presence of aniline	In presence of m-toluidine	In presence of o-toluidine	In presence of p-toluidine
5	9.21	7.9	3.7	7.4	20.0
15	35.52	20.7	8.6	17.5	50.0
25	84.21	29.7	17.7	27.7	78.0
35	97.36	34.6	17.7	36.1	85.0
45	100.00	44.5	22.0	40.7	89.0
55	–	51.4	24.48	46.2	90.0
65	–	54.4	24.48	53.7	93.0

We tested aniline and other amines as inhibitors of oxidation of sodium sulfate. The results obtained are presented in Table 2.

TABLE 3

Time (min.)	Percent oxidation of sodium sulfite	
	Pure	In presence of hydroquinone
5	9.21	0.98
15	35.52	1.96
25	84.21	2.94
35	97.36	2.94
45	100	–

As the data in Table 2 show, m-toluidine had the greatest inhibitory effect upon sodium sulfite oxidation; aniline and o-toluidine were of medium effect; and p-toluidine the least

Ivanov [9] refers to hydroquinone as an inhibitor of isopropyl ether oxidation, and Mekhrov [10] as the most powerful inhibitor against oxidation of fish and sea-mammal fats by atmospheric oxygen. Hydroquinone is also an inhibitor of benzaldehyde [11] and hypophosphorous acid oxidation [12]. We established that hydroquinone is a powerful inhibitor of sodium sulfite oxidation (Table 3).

SUMMARY

The sources cited in the literature and the results of additional experiments testify to the wide applicability of inhibitor action. Phenol inhibits the oxidation of sulfur dioxide, tin sulfate, chloroform and rubber. Sulfur dioxide inhibits the oxidation of phenol. Agerite and neozone inhibit oxidation of rubber and sodium sulfite. Aniline and other amines inhibit the oxidation of rubber, divalent tin, divalent iron, benzaldehyde, and sodium sulfite. Hydroquinone inhibits oxidation of isopropyl ether, fish and sea-mammal fats, hypophosphorous acid and sodium sulfite.

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HYDROLYSIS OF UREIDO ACIDS

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One of the intermediary compounds of ureide derivatives are the ureido acids, $HOOC-R-CO-NHCO-NH_2$, which result from the interaction of dibasic acid anhydrides with urea at the melting temperature of the anhydride [1].

The purpose of this work was a study of the hydrolyzability of ureido acids, and in particular, of maleureido, succinureido and phthalureido acids. Results of such investigation ought to help clarify the resin formation process which takes place in aqueous solution upon interaction of ureido acids with formaldehyde.

It was established from the experimental results that at temperatures below 70° in aqueous solution, hydrolysis of ureido acids is almost non-existent. With an increase in temperature, a reaction leading to the formation of dibasic acids and urea was observed for the first stage.

A study of the hydrolysis kinetics indicated that hydrolysis reactions for succinuerido, maleureido and phthalureido acids, found to be bimolecular, correspond, in the case of a dilute solution, to a first order equation. Calculation of the rate constant was carried out according to the first order reaction formula $K = \frac{2.303}{\tau} \log \frac{C_0}{C}$, where $C < C_0$, in which account was taken of the fact that in the case of ureido acid hydrolysis, the number of milliliters of sodium hydroxide will characterize the reaction of new carboxyl group formation and $V_1 > V_0$.

Hence $\frac{V_1 - V_0}{V_0} = \frac{\Delta C}{C_0}$ and $\frac{C}{C_0} = \frac{2V_0 - V_1}{V_0}$. Substituting, we get $K = \frac{2.303}{\tau} \log \frac{V_0}{2V_0 - V_1}$.

Rate constants, calculated according to this equation, were: for 0.01 N solution of succinuerido acid at 100° = 0.00055; for 0.00977 N solution of maleureido acid at 80° = 0.00162, and at 98° = 0.00277; for 0.01086 N solution of phthalureido acid at 98° = 0.00268.

Hydrolysis of a ureido acid is found to be a gradual process. The urea which is formed in the first stage decomposes further to ammonia and carbon dioxide. For a dilute solution (concentration of 0.01 N), at a temperature of about 80°, the amount of urea decomposing is negligible, and the amount of evolving ammonia is greater than the range of experimental error. In concentrated solutions, for example of maleureido acid, and at 100° and above, the ammonia formed by hydrolysis decreases the total acidity of solution, interacting first with formation of ammonium salt, and second, with maleureido acid molecules which are being formed, giving an acid and intermediate salts.

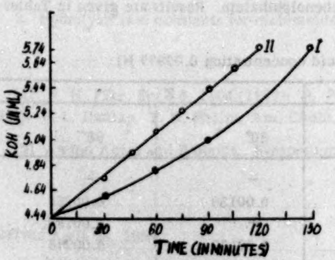

Fig. 1. Relation of hydrolysis rate for 0.00977 N maleureido acid to that of temperature.

I - 80°, II - 98°.

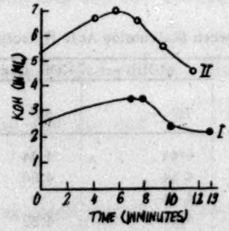

Fig. 2. Relation of hydrolysis rate of maleureido acid to time

I - 0.05 N solution

II - 0.1 N solution

On the basis of what has been stated above, the shape of the curve which characterizes hydrolysis of maleureido acid at 98° differs from that at 80° (Fig. 1), and the curves characteristic for decomposition of maleureido acid in 0.05 N solution, and more concentrated solutions, pass through a maximum (Fig. 2) upon prolonged heating.

The salts of maleureido acid are more stable to hydrolysis than the free acid. Sodium and potassium salts (0.01 N solutions), are practically unaffected by heating for 150 minutes at 99°. The stability of the salt, however, is determined by the nature of the metal which is substituted for the carboyxl hydrogen. Thus, lithium salts under similar conditions are noticeably hydrolyzed.

This can be explained on the basis of mutual influence of atoms, as well as by variation in volume of the metallic atoms which replace the hydrogen. The larger the atomic volume of an element, the more it will hinder attraction of water molecules, which are necessary for the peptide bond, analogous to break-down of polypeptides [2].

Various ureido acids hydrolyze at various rates. Thus the nature of the radical – the radical of the dibasic acid bound to the –CONH– group – also has an influence upon stability of the peptide bond in molecules of ureido acids.

EXPERIMENTAL

Synthesis of Succinureido Acid. 20 g of succinic anhydride and 12 g of urea were heated on an oil bath at 120° for 30 minutes to complete solidification of the molten mass. The substance, recrystallized from hot water, was dried to constant weight. Yield of acid was quantitative.

Found %: N 17.40, 17.45(Kjeldahl). $C_5H_8O_4N_2$. Calculated %: N 17.49. Found: Acid number 348.3. Calculated: Acid number 349.7.

Synthesis of Maleureido Acid. 20 g of maleic anhydride and 12 g of urea were heated in a round-bottomed flask at 60° for 45 minutes, with stirring. Having increased temperature to 80°, heating was continued for another 15 minutes until the entire mass had completely solidified. After recrystallizing from hot water, and drying to constant weight, maleureido acid resulted in quantitative yield.

Found %: N 17.60, 17.55. (Kjeldahl). $C_5H_6O_4N_2$. Calculated %: N 17.7. Found: Acid number 353.4, 354.8. Calculated: Acid number 354.

Synthesis of Phthalureido Acid. 26 g of phthalic anhydride and 10.5 g of urea were heated at 120° for 20 minutes to complete solidification of the entire mass. Aftercrystallization and drying, phthalureido acid resulted in quantitative yield.

Found %: N 13.52, 13.60(Kjeldahl). $C_9H_8O_4N_2$. Calculated %: N 13.45. Found: Acid number 266, 267.5. Calculated: Acid number 268.9.

Hydrolysis Procedure. A flask containing 10 ml. of water was placed in a thermostat. After heating the water to the required temperature, a batch of the acid was added and the mixture stirred vigorously to complete dissolution. A sample was then taken for determination of initial acidity, and the stop-watch then started. Acidity determination was carried out with 0.0111 N solution of potassium hydroxide, using phenolphthalein. Results are given in Tables 1-5.

TABLE 1

Relation Between Maleureido Acid Hydrolysis and Temperature (Acid concentration 0.00977 N)

Duration of experiment (in minutes)	Milliliters of KOH used for neutralization			K	
	70°	80°	98°	80°	98°
0	4.44	4.44	4.44	–	–
30	4.44	4.60	4.74	0.00159	0.00260
45	4.44	–	4.92	–	0.00280
60	4.44	4.82	5.08	0.00163	0.00278
75	4.44	–	5.22	–	0.00276
90	4.44	5.02	5.38	0.00165	0.00278
105	4.44	–	5.58	–	0.00284
120	4.44	–	5.74	–	0.00262
135	4.44	5.74	–	0.00161	–
			Average..................	0.00162	0.00277

TABLE 2

Relation Between Maleureido Acid Hydrolysis and Time at 98°

Time (in hours)	Milliliters of KOH (0.08547 N) to neutralize the 0.05 N solution of acid.	Time (in hours)	Milliliters of KOH (0.08547 N) to neutralize the 0.1 N solution of acid.
0	2.65	0	5.3
7	3.4	4	6.6
8	3.55	5.5	6.9
10	2.3	7.5	6.5
13	2.2	9.5	4.5
		11.5	

TABLE 3

Hydrolysis of 0.01 N Solution of the Lithium Salt of Maleureido Acid

Time (in minutes)	0.0111 N KOH (in ml)
15	0
30	0.04
45	0.05
60	0.06
90	0.07
120	0.08
150	0.1

TABLE 4

Hydrolysis of 0.01 N Solution of Succinureido Acid at 100°

Time (in minutes)	0.011 N KOH (in ml)	K
0	4	–
45	4.10	0.00055
60	4.14	0.00057
75	4.16	0.00055
90	4.18	0.00051
120	4.26	0.00056
135	4.30	0.00057
150	4.32	0.00055
	Average	0.00055

TABLE 5

Hydrolysis of 0.01086 N Solution of Phthalureido Acid at 98°

Time (in minutes)	0.011 N KOH (in ml)	K
0	4.9	–
30	5.24	0.00240
45	5.40	0.00239
60	5.6	0.00255
90	6.24	0.0034
	Average........	0.00268

Among the hydrolysis products of maleureido acid which was heated for a prolonged period, were found maleic acid and the ammoniacal salt of maleureido acid. 0.05 N maleureido acid solution, heated for 8 hours, was then extracted repeatedly with ether. From the ether extract a product, m.p. 130°, crystallized out. A sample mixed with known maleic acid did not give depression. The solution, treated with ether, was evaporated to the point of crystallization. After drying, there resulted crystals of the ammoniacal salt of maleureido acid.

Found %: N 24.2 (Kjeldahl). $C_5H_9O_4N_3$. Calculated %: N 24.00.

SUMMARY

1. Hydrolyzability of malerueido acid, its salts, of succinureido and of phthalureido acids, has been investigated.

2. Hydrolysis rate constants for maleureido, succinureido and phthalureido acids have been determined.

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REACTION OF ETHYLENE CHLOROHYDRIN WITH 2,5-DICHLOROANILINE AND ANILINE

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We have previously demonstrated [1] that the reaction of ethylene chlorohydrin with 2,5-dichloroaniline, accompanied by the production of N-ethanol-2,5-dichloroaniline (2,5-dichlorophenylethanolamine) does not proceed as maintained by Krasussky, via a stage in which ethylene oxide is formed,then to react with amine, but by direct exchange of a halide for an amino group. This was confirmed by the fact that ethylene oxide in isolation does not react with 2,5-dichloroaniline.

The present study had the purpose of clarifying whether 2,5-dichloroaniline would react with ethylene oxide at the moment of its production. Toward that end we set up the following experiment. Into an apparatus containing 2,5-dichloroaniline and a solution of caustic soda, we gradually poured ethylene chlorohydrin, which, as is known [2], reacts immediately with caustic soda, producing ethylene oxide; it appeared thereby that the ethylene oxide produced under these conditions of experiment, did not react with 2,5-dichloroaniline and left the reaction zone. This was also confirmed by a control experiment so conducted that the ethylene oxide produced from ethylene chlorohydrin and leaving the reaction zone, was caught in a trap containing aniline. Monoethanolaniline was accordingly produced in the trap where the ethylene oxide underwent absorption by aniline. But the control experiment also failed to produce N-ethanol-2,5-dichloroaniline. It follows, therefore, that ethylene oxide does not react with 2,5-dichloroaniline at the moment of its formation.

The reaction of ethylene chlorohydrin with aniline was studied in passing in this investigation. It is known that reaction of ethylene chlorohydrin with aniline and its derivatives is usually accomplished by heating these substances, mixing them the while [2-4]. Shorygin, Smirnov and Belov [5,6] describe this process as taking place in the presence of water, which increases the yield of monoethanolaniline (80%). In this procedure, the separation of monoethanolaniline from the reaction mixture is performed in the usual way [2-6].

Unlike the foregoing, Rindfus and Harnack [7] conducted this reaction in presence of soda and obtained monoethanolaniline and diethanolaniline simultaneously, although they did not indicate the yields of these products. Nevertheless, this approach is of definite interest, as it is capable of being used for the synthesis of diethanolaniline and other dialkanolanilines.

Judging by our observations, however, the ethylene chlorohydrin reaction with aniline should preferably be conducted not in the presence of soda, as soda tends to cause hydrolysis of ethylene chlorohydrin into ethylene glycol [2], but in the presence of chalk, caustic soda or lime. When this is done, the experiments show that the reaction proceeds chiefly in the direction of the production of the ethanol derivatives of aniline. *

We obtained analogous results in synthesizing diethanolaniline. In this instance we used a 2.2 : 1 ratio of initial ethylene chlorohydrin and aniline, with the result that when reacted in the presence of chalk the diethanolaniline yield was 79.22% of theory, and 83.04% when conducted in the presence of caustic soda.

In addition, for purposes of comparison we attempted to obtain diethanolaniline (without use of alkali and chalk) by heating 2.2 mole of ethylene chlorohydrin with 1 mole of aniline in the presence of 10 ml water. It turned out, however, that in this instance the reaction proceeded mainly to the production of monoethanolaniline. Diethanolaniline was produced in but an insignificant quantity, and we did not succeed in isolating it from the reaction mixture in pure form.

As far as the mechanism of the reaction of ethylene chlorohydrin and aniline are concerned, when this process occurs in the presence of chalk and alkalis, which readily convert ethylene chlorohydrin into ethylene oxide [2,8], the reaction probably does proceed chiefly through the stage of oxide formation and its subsequent reaction with aniline. However, this does not contradict Krasussky's rule [9], which established in terms of the reactions of isomeric α -monochlorohydrins that under ordinary circumstances, i.e., in the absence of alkalis, "the formation of α -aminoalcohols from α-monochlorohydrins proceeds through α -oxides", constituting intermediate products in the reaction of ammonia and the amines with α -monochlorohydrins.

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* Thus, for example, by heating 1 mole of ethylene chlorohydrin with 2 moles of aniline in the presence of chalk, we obtained an 83% yield of monoethanolaniline.

However, it is not impossible that the production of monoethanolaniline and diethanolaniline from aniline and ethylene chlorohydrin may also take place to some degree by direct exchange of a halide for an amino group, as, for example, in the derivation of N-ethanol-2,5-dichloroaniline from 2,5-dichloroaniline and ethylene chlorohydrin [1].

EXPERIMENTAL

Effort to obtain N-ethanol-2,5-dichloroaniline from 2,5-dichloroaniline and ethylene oxide at the moment of its formation. 162 g 2,5-dichloroaniline, 40 g caustic soda and 100 ml water were heated to boiling, stirred constantly, and 80.5 g ethylene chlorohydrin was then poured gradually into the mixture. N-Ethanol-2,5-dichloroaniline was not obtained. The results of this experiment show that ethylene oxide at the moment of its formation does not react with 2,5-dichloroaniline, but does react with aniline (280 g) in the trap at 100 g, giving monoethanolaniline. The monoethanolaniline thus formed was separated from the aniline by fractionation in vacuum. The aniline was driven off in a column. The remainder was redistilled from a Claisen retort. When this was done, the monoethanolaniline fraction (25.2 g) was collected within 147-148°/8 mm:

d_{20}^{20} 1.0942, n_D^{20} 1.5780 [10].

Found %: N 10.2. $C_8H_{11}ON$. Calculated %: N 10.21.

Production of monoethanolaniline and diethanolaniline from aniline and ethylene chlorohydrin in the presence of caustic soda. The ethylene chlorohydrin and aniline were placed in a three-necked flask provided with a stirrer and a reflux condenser, and heated to 100°. A solution of caustic soda was then gradually added to the mixture in the course of 7 or 8 hours through a dropping funnel. The reaction was conducted in an oil bath whose temperature was maintained at between 100 and 110° throughout the entire process.

Data on the Production of Mono- and Diethanolaniline

Experiment No.	Charge (g)								
	Aniline	Ethylene chlorohydrin	Chalk/water (ml)	NaOH/water (ml)	monoethanolaniline•			diethanolaniline	
					yield (in %)	b.p./4-5 mm	n_D^{20}	yield (in %)	m. p.
1	186	80.5	–	40/150	78.72	135–145°	1.5805	–	–
2	93	177.1	–	88/330	–	–	–	83.04	51–52°••
3	232.5	80.5	62.5/100	–	83	134–138	1.5800	–	–
4	93	177.1	120/100	–	–	–	–	79.22	53–55

• Constants of product obtained correspond to data in literature [10].

•• After recrystallization from benzene the diethanolaniline consists of white needles of m.p. 57-58° [11]. Found %: N 7.74. $C_{10}H_{15}O_2N$. Calculated %: N 7.73.

At the end of the process the reaction products were separated off from the water layer and fractionated in vacuum. The results of distillation of monoethanolaniline are given in the table (Experiment 1). Diethanolaniline was collected between 185 and 195° at 3 mm; upon standing it congealed into a yellow crystalline mass (Experiment 2).

Production of monoethanolaniline and diethanolaniline from aniline and ethylene chlorohydrin in the presence of chalk. Ethylene chlorohydrin from a dropping funnel was gradually added in 2 hours to a mixture of aniline, chalk and water heated to 80-100°, stirring being constant. The mixture was then heated to boiling and mixed for another 8 to 14 hours.

When monoethanolaniline was produced (Table, Experiment 3), the product was suction filtered out of the mineral residue at the end of the reaction, separated from the water layer and fractionated in a vacuum.

When diethanolaniline was produced (Experiment 4), the reaction mass was diluted with 200 ml water and 300 ml benzene for ease of filtration. Upon fractionation, the diethanolaniline fraction was collected between 165 and 169°/1.5 mm. When allowed to stand, the product formed a yellow crystalline mass.

SUMMARY

This study confirmed the opinion we had advanced previously that the formation of N-ethanol-2,5-dichloroaniline from 2,5-dichloroaniline and ethylene chlorohydrin proceeds not by Krasussky's rule, but by direct exchange of a halide for an amino group. At the same time is was shown that the formation of ethanol derivatives of aniline from aniline and ethylene chlorohydrin in the presence of chalk and caustic soda takes place for the most part through a stage in which ethylene oxide is formed, which then reacts with amino, i.e., as stated by Krasussky.

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TRANSETHERIFICATION OF DIALKYLAMINOMETHYLAKYL ETHERS AND DIALKYLAMINOMETHYLALKYL SULFIDES

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Having proved the ability of dialkylaminomethylalkyl ether mixtures (I) [1] to exchange alkoxyl groups at elevated temperatures, we regarded it as of interest to study this reaction in mixtures of ethers (I) with their sulfide analogs – the dialkylaminomethylalkyl sulfides $\begin{matrix}R\\R\end{matrix}\!\!>\!NCH_2SR'$ (II). The work of Prilezhaeva, Shapiro and Shostakovsky [2], demonstrating the ability of the α,β-dialkoxydiethylsulfides, with monothioacetal structure, to take on symmetry with heating or in presence of acids, with the formation of equimolecular quantities of dialkylacetals and dialkoxydiethyl mercaptals, made it possible to postulate the transetherification of mixtures of ethers (I) and (II) sulfides. These sulfides (II) were first synthesized by McLeod and Robinson [3] by reacting dialkylamine, mercaptan and an aqueous solution of formaldehyde, but received no further study by anyone. The only chemical property of these compounds noted was the fact that the sulfides were more stable to hydrolysis than the ethers (I). While diethylaminomethyl ethyl ether decomposes to a secondary amine, formaldehyde and alcohol, when merely shaken with cold water, diethylaminomethylisopropyl sulfide hydrolyzes slowly only under the action of hot water.

We obtained the initial dialkylaminomethylalkyl sulfides by heating the ethers (I) with mercaptans in conditions analogous to those we had described earlier for reacting ethers (I) with alcohols.

This method permitted the reaction to proceed in a homogenous medium without a solvent, which was particularly convenient in working with high-molecular mercaptans, virtually insoluble in water. When diethylaminomethyl ethyl ether (III) was heated with n-octyl- and n-decylmercaptans, we obtained diethylaminomethyl-n-octyl sulfide (IV) and diethylaminomethyl-n-decyl sulfide (V), in yields, respectively, of 91 and 80% of the theoretical.

The synthesized dialkylaminomethylalkyl sulfides (IV) and (V) were employed in transetherification reactions with ethers (I).

An equimolecular mixture of piperidinomethyl ethyl ether and (IV) was heated in a sealed ampoule for 40 hours at 140°. After fractionated vacuum distillation, the dark, free-flowing liquid resulting from the reaction gave both expected reaction products: diethylaminomethyl ethyl ether (III) (yield 34.6% of theoretical) and piperidinomethyl-n-octyl sulfide (VI) (yield 37.6% of theoretical)

$$C_5H_{10}NCH_2OC_2H_5 + \underset{(IV)}{(C_2H_5)_2NCH_2SC_8H_{17}} \rightarrow \underset{(VI)}{C_5H_{10}NCH_2SC_8H_{17}} + \underset{(III)}{(C_2H_5)_2NCH_2OC_2H_5}.$$

Heating of a mixture of diethylaminomethyl-n-decyl sulfide (V) and piperidinomethyl ethyl ether under the same conditions gave piperidinomethyl-n-decyl sulfide (VII) (yield 30% of theoretical) and ether (III).

Thus, it may be taken as proved that the heating of a mixture of dialkylaminomethyl alkyl ether and dialkylaminomethylalkyl sulfide causes exchange of alkoxyl and alkyl sulfide groups.

All the sulfides described (IV, V, VI and VII) were here produced for the first time. They are free-flowing, colorless liquids with strong and unpleasant odor, undergo vacuum distillation without decomposition, are readily soluble in organic solvents and virtually insoluble in water.

EXPERIMENTAL

Diethylaminomethyl-n-octyl sulfide (IV). A mixture of 29.2 g n-octyl mercaptan (0.2 mole) and 28.8 g ether (III) (0.22 mole) was heated to 130° in a three-necked bottle, equipped with stirrer, thermometer and descending condenser. Ethyl alcohol began to be given off at that temperature. Within an hour and a half the temperature of the reaction mass reached 170°, when distillation ended. The total amount of ethyl alcohol given off was 7.1 g, containing 0.7% of nitrogenous compounds (recalculated as nitrogen).

Fractionated vacuum distillation of the reaction mass gave 42.4 g of sulfide (IV) (91.6% of the theoretical).

B.p. 134°/6 mm, d_4^{20} 0.8678, n_D^{20} 1.4692, MR_D 74.30; calculated 83.54.

4.820 mg substance: 11.968 mg CO_2; 5.410 mg H_2O. 4.840 mg substance 11.992 mg CO_2; 5.506 mg H_2O. 4.468 mg substance: 1.908 ml 0.02 N $Na_2S_2O_3$. 0.4778, 0.4750 g substance: 19.90, 19.80 ml 0.1N HCl. Found %: C 67.76, 67.61; H 12.56, 12.72; S 13.68; N 5.83, 5.84. $C_{13}H_{29}NS$. Calculated %: C 67.46; H 12.63; S 13.86; N 6.05.

Diethylaminomethyl-n-decyl sulfide (V). A mixture of 10.45 g n-decylmercaptan and 3 g (III) was heated until ethyl alcohol began to be given off; at that temperature (125-128°) another 5.7 g (III) was added in the course of an hour. It was then heated for two hours at 140-145° until distillation ceased (1.8 g; 1.0% content nitrogen compounds). Fractional vacuum distillation of the reaction mixture gave 12.4 g (V) (79.7% of the theoretical).

B.p. 167-169° at 5 mm, d_4^{20} 0.8672, n_D^{20} 1.4683, MR_D 83.21; calc. 83.54.

7.554 mg substance: 19.298 mg CO_2; 8.582 mg H_2O; 2.700 mg SO_4. 6.850 mg substance: 17.495 mg CO_2; 7.808 mg H_2O; 2.500 mg SO_4. 0.2478, 0.2708 g substance: 9.27, 10.13 ml 0.1N HCl. Found %: C 69.71, 69.70; H 12.71, 12.75; S 11.93, 12.18; N 5.24, 5.22. $C_{15}H_{33}NS$. Calculated %: C 69.42; H 12.82; S 12.36; N 5.40.

Transetherification of diethylaminomethyl-n-octyl sulfide (IV) and piperidinomethyl ethyl ether. A mixture consisting of 17.32 g sulfide (IV) and 10.72 g piperidinomethyl ethyl ether was heated in a sealed ampoule at 140° (in xylol vapor) for 40 hours. The reaction mass darkened noticeably. Two main fractions were obtained after fractional vacuum distillation: 1st, b.p. 57-62° at 20 mm, 6.1 g; 2nd, b.p. 156-157° at 8 mm, 13.5 g. Distillation of the 1st fraction under normal pressure in a laboratory rectification column gave 3.4 g ether (III) (34.6% of theoretical) with b.p. 132-133°. According to the literature on (III) its b.p. is 132-134° [4].

Found %: N 10.63, 10.54. $C_7H_{17}ON$. Calculated %: N 10.68.

Vacuum redistillation of the 2nd fraction gave 6.85 g of sulfide (VI) (37.6% of the theoretical).

B.p. 159-160° at 6 mm, n_D^{20} 1.4887, d_4^{20} 0.9105, MR_D 77.12; calc. 76.72.

5.472 mg substance: 13.820 mg CO_2; 5.882 mg H_2O. 4.136 mg substance: 10.432 mg CO_2; 4.468 mg H_2O. 3.880 mg substance: 1.583 ml 0.02 N $Na_2S_2O_3$. 3.451 ml substance: 1.421 ml 0.02 N $Na_2S_2O_3$. Found %: C 68.97, 68.82; H 12.03, 12.09; S 13.08, 13.20. $C_{14}H_{29}NS$. Calculated %: C 69.06; H 12.01; S 13.17.

Transetherification of diethylaminomethyl-n-decyl sulfide (V) and piperidinomethyl ethyl ether. A mixture of 8 g sulfide (V) and 4.4 g piperidinomethyl ethyl ether was heated and processed as above.

The result of fractional vacuum distillation was the recovery of 0.7 g ether (III) and 2.5 g (30%) sulfide (VII).

B.p. 150-152° at 3 mm, n_D^{20} 1.4831.

5.360 mg substance: 13.908 mg CO_2; 5.889 mg H_2O. 5.446 mg substance: 14.088 mg CO_2; 5.978 mg H_2O. 3.815 mg substance: 1.421 ml 0.02 N $Na_2S_2O_3$. Found %: C 70.81, 70.59; H 12.30, 12.28; S 11.94. $C_{16}H_{33}NS$. Calculated %: C 70.78; H 12.25; S 11.81.

SUMMARY

1. The production of dialkylaminomethylalkyl sulfides by reacting dialkylaminomethyl alkyl ethers with mercaptans was demonstrated to be possible.

2. It was shown that heating of a mixture of dialkylaminomethyl alkyl ethers and dialkylaminomethylalkyl sulfides resulted in the exchange of alkoxyl and sulfhydryl groups.

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EFFECTS OF VARIOUS CATALYSTS UPON THE DIRECTION AND RATE OF BROMINATION OF AROMATIC COMPOUNDS

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It is known that chlorination and bromination of benzene, depending upon conditions of the reaction, proceeds in one of two directions. In the presence of ferric or aluminum halide, and many other catalysts, substitution of hydrogen atoms takes place; in light, or in the presence of sodiumcarbonate, halogen addition takes place. Replacement of hydrogens on carbon atoms of the benzene ring for benzene homologs is promoted by the same catalysts as for benzene itself; in light and with heating, as well as in the presence of phosphorous halides, substitution in the side chain predominates [1].

After comparing a number of factors, the conclusion can be reached that the benzene molecule itself enters more readily into an addition reaction than into a substitution reaction. This was definitely proved for the chlorination of benzene by N. N. Vorozhtsov [2]. For the homologs of benzene, substitution of hydrogen in the side chains proceeds most readily. Light and heat are the physical factors which on the whole cause weakening and rupture of the bonds, under which conditions those bonds which are weak rupture most readily. Catalysts which promote substitution in the benzene ring are substances of the electron-accepting type. They, or their complexes with other components of the reacting mixtures (for example with halogens, organohalogen compounds, etc.) add in a complex way to carbon of the benzene ring, weakening the carbon-hydrogen bond to such an extent that this bond is more readily ruptured than any other bonds in the molecule. The effect of sodium carbonate upon the direction of chlorination and bromination of benzene can be explained as follows: upon reaction of halogen with benzene, the addition reaction occurs more readily, but substitution of hydrogen can also proceed to a small extent; the evolving HCl or HBr reacts with their proton as an electron-accepting catalyst, accelerating substitution; sodium carbonate, however, neutralizes the hydrogen halide [3]. In similar fashion should act water, which physically removes hydrogen halide from the area of reaction. Upon halogenation of benzene homologs, water and sodium carbonate should promote substitution in the side chain. Hence it might also be expected that in the presence of water and other substances, which promote addition in the benzene ring and substitution in the side chains of homologs, that the halogenation reaction would proceed more slowly. As far as the standard catalysts are concerned, the more a given catalyst accelerates the reaction, the more substitution in the ring should predominate over other directions of chlorination and bromination.

The main purpose of the present work was to reexamine these positions.

Benzene bromination experiments carried out without additives, as well as in the presence of dry hydrogen bromide and water, have indicated that HBr accelerates the reaction noticeably, and that water decelerates the reaction. Acetic acid, which can bind HBr, converting it into a complex, inhibits the bromination reaction somewhat, but does not remove the HBr from the sphere of reaction because it mixes with benzene.

Determination of the benzene bromination rate at room temperature was carried out with a large number of catalysts of positive and negative actions. For the experiments, simple materials were taken for the most part, which converted into bromide in the reaction process. The average temperature was 18°, with the same fluctuation in all experiments.

The highest acceleration of bromination was observed with the action of iron and of zinc. Bi, Cu, Hg, Pb, Mg, Cd, Te, Mo, Sn were not so effective. I, Co, Al, Sb, Mn, Ni displayed even less activity. P, As, S, Se were found to be very weak catalysts. Nitro compounds inhibited benzene bromination somewhat; iodobenzene accelerated bromination of benzene noticeably.

Toluene reacted more rapidly than benzene. Arrangement of catalysts in order of their power of action approximated on the whole that observed with benzene. Fe and Zn accelerated bromination the most; HBr accelerated somewhat, but water did not inhibit. Chlorobenzene brominated more slowly with a majority of the catalysts than did benzene, but with tellurium, brominated more rapidly. Nitrobenzene reacted very slowly, while a stronger accelerating action was observed for Bi and for Zn at the beginning of the reaction; however, over a longer time, interaction was accelerated more significantly by Al, S, Fe.

In experiments with simple compounds, measurements of reaction rates were complicated by the fact that such compounds converted into bromides not at a uniformly rapid rate. This apparently explains the variation in course of the process. At times bromination proceeded quite uniformly, and at times with a sharp change in rate one way or the other. Thus, with mercury, only 2.7% bromine was used within the first day, and 94.6% after 50 days; with copper the figures were, respectively, 81.5 and 84%, and for iodobenzene, 39.3 and 43.8%.

More clear-cut results in the sense of comparison of the activities of catalysts should be given from experiments with commerical bromides. Such an investigation was carried out by the authors for only a few catalysts, and for each catalyst only one experiment was carried out. Bromination of benzene was carried out in a thermostat (temperature 45°). The catalysts were arranged by strength of action in the following order: $FeBr_3 > AlBr_3 > ZnBr_2 > IBr_3 > SbBr_3 > AsBr_3 > CuBr_2 > S_2Br_2 > PBr_5$. Here of special interest was the low activity of zinc and of copper bromides. This is related, it is thought, to the fact that other bromides were in solution, while $ZnBr_2$ and $CuBr_2$, as separate experiments indicated, are insoluble in benzene. Hence, in this case the catalysis possessed a heterogeneous character, and the reaction rate depended to a great extent upon powdering of the catalyst. The bromides were simply ground to a powder, and in experiments with metallic zinc and copper, the latter were taken in the finely powdered state.

Zinc in the form of dust can be recommended for practical use in the bromination of benzene in organic synthesis laboratories. In a majority of the manuals for synthesis of organic compounds, benzene bromination in the presence of iron is proposed. Ortner and Reichel [4] recommend pyridine for the catalyst. Having noticed a high activity for zinc, the authors carried out the reaction under identical conditions with all three catalysts Fe and Zn gave the same quantitative yield of C_6H_5Br with negligible amounts of dibromobenzene; however, with pyridine there resulted 68.4% C_6H_5Br and 8% $C_6H_4Br_2$. Zinc had the added advantage over iron that $ZnBr_2$ is colorless and does not hydrolyze readily; these facts facilitated subsequent treatment of the reaction mixture. Experiments with different amounts of zinc dust indicated that to obtain good results it is sufficient to take 0.005 to 0.01 g at. wt. of zinc per mole of bromide.

Results of determination of reaction products upon bromination of benzene and toluene with different additives, confirmed, on the whole, the initial hypotheses. Those catalysts which accelerate bromination promote substitution of hydrogen on the benzene ring, and, as a rule, the percentage of bromobenzene or of bromotoluenes in the bromination product is higher, the stronger the catalyst. On the whole, however, there is not observed here a strict parallelism. Additives which inhibit the reaction, in the case of benzene, direct to a considerable degree toward addition, and with toluene, in the direction of substitution in the methyl group.

EXPERIMENTAL

I. Determination of Benzene Bromination Rate in the Presence of HBr, H_2O, CH_3COOH. A mixture of benzene and bromine in the ratio of 0.02 mole bromine to 1 mole of benzene was divided into 5 portions. One portion was left as a control, gaseous HBr was passed into a second portion to a concentration of 0.05 mole per mole of Br_2, in a third portion HBr was dissolved to a content of 0.1 mole per mole of Br_2, to a fourth portion was added H_2O, and to the 5th portion was added CH_3COOH of the same molecular concentration. All solutions were left to stand in the dark at room temperature. Samples were removed from each, which, after addition of KI, were titrated with sodium thiosulfate. Results are given in Table 1.

TABLE 1

Bromination of Benzene in the Presence of HBr and H_2O

Catalyst	Amount of reacted bromine (in %) with prolonged period for experiment.									
	3 days	8 days	18 days	38 days	5 mo.	13 mo.	16 mo.	17 mo.	18 mo.	22 mo.
Without catalyst	2.6	5.7	7	13.3	25.7	28.4	32.5	39.5	39.5	100
HBr (0.05 mole)	–	5.3	8	16.7	–	41.1	42.9	–	–	–
HBr (0.1 mole)	2.7	10.8	11.2	18.8	31	55.3	57.9	65.8	100	–
H_2O (0.1 mole)	4.2	4.6	7.4	7.4	7.9	8.5	10.6	12.7	–	55.8
CH_3COOH (0.1 mole)	5	7.4	8.7	10.1	15	16.3	56.8	58	–	–

100% bromine was used with water for 30 months, and with CH_3COOH for 28 months.

II. Determination of Bromination Rate of Aromatic Compounds in the Presence of Various Catalysts. A mixture of benzene with bromine in the molecular ratio 50 : 1 was divided into portions, to which were added positive and negative catalysts in the amount of 0.01 mole per mole of bromine. All mixtures were left at room temperature. From them aliquots were taken in which unreacted bromine was determined iodometrically. The data obtained are given in Tables 2 and 3.

Toluene (Table 4), chlorobenzene (Table 5) and nitrobenzene (Table 6) were treated under similar conditions.

III. Bromination of Benzene In the Presence of Bromides of Certain Elements. Benzene and bromine were taken in the amounts of 35 and 10.1 ml., i.e., in the molecular ratio of 2 : 1, catalyst in the amount of 0.01 mole per mole of bromine. Reaction was carried out at 45° for 10 hours. Constancy of temperature was maintained within 0.2° by a thermostat regulated by a mercury-toluene regulator. After completion of the experiment, unreacted bromine was removed by shaking with a 10% solution of NaOH, and the mixture washed several times with distilled water, dried with $CaCl_2$ and fractionated twice, the second time with a dephlegmator. As a result the mixture was sharply divided into two fractions: 80-83° (benzene) and 155-157° (bromobenzene). The residue in the flask was taken to be a mixture of dibromobenzenes. Since losses are unavoidable during treatment of the reaction mixture, an experiment was therefore carried out with a mixture of 10 ml of C_6H_6 and 20 ml of C_6H_5Br without catalyst.

After washing the above-mentioned mixture with alkali and water, drying with $CaCl_2$ and two fractionations, there resulted 18 ml. of bromobenzene, i.e., losses amounted to 10%. The results are given in Table 7.

IV. Effects of Temperature and Quantity of Catalyst on the Bromination Rate of Benzene in the Presence of Zinc. The resulting data are given in Tables 8 and 9.

V. Some Preliminary Experiments on Bromination of Aromatic Compounds with Various Catalysts. 1) 22 ml (0.25 mole) of C_6H_6, 10 ml (0.2 mole) of bromine and 0.09 gram at. wt. of Fe powder. Reaction was carried out with heat on a water bath at 40-45°; 31 g of bromobenzene resulted, i.e., about 100% of theoretical yield, with traces of dibromobenzenes.

2) The same quantities of reactants, and experimental conditions, were used, but in place of iron, zinc dust was used. Yield of C_6H_5Br was theoretical.

3) The same, with pyridine as a catalyst. Yield of bromobenzene was 68.4% of theory, p-dibromobenzene was 8%.

4) The same, with C_6H_5I catalyst: yield was 40% for C_6H_5Br, and 6.9% of p-$C_6H_4Br_2$.

5) Same without catalyst: yield of C_6H_5Br 31%.

6) 26.5 ml (0.25 mole) of $C_6H_5CH_3$, 10 ml of Br_2 were taken. Reaction time was 5 hours. Yield (in %) of bromotoluene was 88, of benzyl bromide, 12.

7) The same, with 0.57 g (0.09 g at. wt.) of zinc, reaction time 1 hour, without heating. 16.6 g (48%) of bromotoluene resulted. $C_6H_5CH_2Br$ was not found.

8) The same, with 79.5 ml of water, reaction time about 5 hours at room temperature. After two fractionations with dephlegmator, 14.4 g of bromotoluenes were obtained, benzyl bromide amounting to 2.7 g.

9) 25.5 ml (0.25 mole) of C_6H_5Cl was taken, 10 ml Br_2 and 0.58 g Zn. Time was 12 hours at 40-50°. Yield of chlorobenzenes mixture was 4.3 g (11.2%).

10) The same, with Fe (0.5 g) catalyst, 1 hour without heating. 19.1 g (50%) resulted.

11) 26 ml. (0.25 mole) $C_6H_5NO_2$, 10 ml of Br_2 and 0.5 g of Fe were taken; time was 30 hours at 50-60°. 0.65 g (1.6%) $C_6H_4BrNO_2$ resulted.

12) The same, with catalyst, S. Same conditions. 0.74 g (1.8%) $C_6H_4BrNO_2$ resulted.

VI. A Study of the Influence of Catalysts Upon the Direction of the Reaction.

1) Experiments with Prolonged Bromination of Benzene. Reaction was carried out at room temperature. The molecular ratio of $C_6H_6 : Br_2 :$ catalyst = 50 : 1 : 0.01. The reaction mixture was treated with water, NaOH solution, and again washed with water. The solution was then dried with $CaCl_2$, the benzene distilled off, and then the C_6H_5Br distilled with steam.

The residue after distilling out the C_6H_5Br should have been, according to the literature data, hexabromocyclohexane: HBr was evolved when the former was heated. The data obtained are given in Table 10.

2) Bromination Products of Toluene. The molecular ratio of $C_6H_5CH_3 : Br_2 :$ catalyst = 50 : 1 : 0.01. Room temperature. Reaction was carried to complete utilization of bromine. The mixture was treated as before, but with direct distillation, without redistillation with steam. The 180-200° fraction, which was found to be a mixture of bromotoluenes and benzyl bromide, was boiled for 40 minutes with an alcoholic solution of KOH, and then diluted with water. The bromotoluenes were extracted with ether, and $AgNO_3$ solution added to an aqueous solution acidified with nitric acid.

The AgBr precipitate was washed, dried on a glass filter at 100° for 5 hours, and weighed. $C_6H_5CH_2Br$ was calculated, and by difference, the amount of $CH_3C_6H_4Br$ was determined. Experimental results are given in Table 11.

TABLE 2

Bromination of Benzene (1st series of experiments)

Duration of experiment	Quantity of reacted bromine (in %) with catalyst													
	Without catalyst	Cu	Mg	Zn	Pb	S	Se	I_2	Fe	H_2O	$C_2H_4O_2$	$C_6H_5NO_2$	$C_6H_4(NO_2)_2$	C_6H_5I
1 hr.	–	79.3	–	85	61.1	–	–	–	88.2	–	–	–	2	–
6 hrs.	–	81.5	58.5	85.7	61.1	–	6	–	89.5	–	–	–	2.56	39.3
1 day	–	81.5	58.5	89.2	61.1	–	6	–	92.1	0	0	–	2.56	39.3
20 days	1.3	83.1	59.4	100	62.3	0.7	–	10	100	0	0	0.7	2.56	40
2 mo.	1.6	83.4	59.8	–	65.3	4.4	6	25.9	–	1.3	2.3	2.3	4.4	41.9
4 mo.	6.7	84	61.7	–	66.8	9.3	7.4	44.9	–	6.1	8.7	8.7	6.8	43.8
7 mo.	9.0	85	62.7	–	71.6	9.7	9	58	–	9.3	13.8	13.8	6.8	45.7

TABLE 3

Bromination of Benzene (2nd series of experiments)

Duration of experiment	Quantity of reacted bromine (in %) with catalyst														
	Without catalyst	Cd	Hg	Al	Sn	P	As	Sb	Bi	Mo	Te	Mn	Co	Ni	$C_6H_2(NO_2)_3OH$
2 hrs.	–	–	1.8	4	–	11.4	8.1	8.1	10	3.2	7.8	0.5	3.2	2.3	–
1 day	1.8	6.4	2.7	4	10	11.4	8.1	8.1	18.2	5.5	8.1	2.8	3.7	3.7	1.0
4 days	1.8	20.5	20	15.5	11.4	–	10	10	38.7	12.7	15.0	4.0	5.5	3.7	1.8
25 days	2.3	54.6	76.4	21	12.8	11.4	10	10	92.8	46.4	46	8.1	9.6	8.2	3.7
50 days	3.7	70	94.6	21	13.2	12.7	11	11	97.8	51.4	58.7	14.6	16	9.6	3.7
4 mo.	5.5	82.8	100	21	17.8	15	15	20	100	63.7	100	25.5	42.8	15.5	–
7 mo.	7.3	86	–	23.2	–	18.2	15	33.7	–	71.9	–	30.5	51.9	19.6	–
14 mo.	8.7	100	–	46.7	72.3	24.1	18.7	49.1	–	80	–	46	59.1	24.1	3.7

TABLE 5

Bromination of Chlorobenzene

Duration of experiment	Quantity of reacted bromine (in %) with catalyst								
	Without catalyst	Mg	Zn	Hg	Al	Bi	Te	S	I	HBr
30 min.	0	1.7	3.3	2.8	1.1	2.8	3.3	1.7	0	2.2
1 hr.	–	–	3.3	2.8	1.1	2.8	10.4	–	0	–
7 hrs.	0.7	1.7	7.2	–	2.2	6.1	83.1	2.8	0	2.2
1 day	1.1	1.7	7.2	2.8	2.2	8.2	89.6	2.8	0	2.8
8 days	1.7	3.3	22.4	7.2	4.4	34.4	100	6.2	0.7	3.9
30 days	1.7	3.3	34.4	10	5	48.6	–	10	5.5	5.0
9 mo.	5.5	6.1	82.6	31.4	14	69.4	–	41	42.8	7.7

TABLE 4
Bromination of Toluene

Duration of experiment	Quantity of reacted bromine (in %) with catalyst																		
	Without catalyst	Cu	Mg	Zn	Cd	Hg	Al	Sn	Pb	Sb	Bi	S	Te	I	Fe	H_2O	HBr	C_6H_5I	$C_6H_4(NO_2)_2$
30 minutes	0	0	0	2.9	1.8	1.7	1.7	0.9	0.6	5.7	0	0	0	0	2.9	0	0	0	0
1 hour	0	–	2.9	32	5.8	8	–	–	–	–	14.3	2.3	1.2	1.7	3.2	0	0	0	0
2 hours	0	9.2	–	70	–	–	17.7	22.9	13.2	15.5	72	–	10.9	–	–	0	18.3	1.8	1.8
5 hours	2.9	26.3	40.3	80.6	4.6	76.6	27.5	33.8	28	18.9	–	24.6	40.6	42.3	100	8	21.2	8.6	5.8
9 hours	–	–	–	100	63.8	100	29.2	55.5	–	–	100	–	68.6	–	–	8	–	9.6	–
1 day	14.9	26.3	61.2	–	89.2	–	42.9	94.9	40	46.3	–	45.8	98.9	77.2	–	14.8	33.2	25.8	14.9
3 days	25.8	45.8	62.3	–	98.9	–	66.9	100	52.3	74.9	–	61.2	100	88	–	25.8	44.5	34	26.9
4 days	42.9	60.6	63.5	–	100	–	89.9	–	57.2	82.9	–	67.6	–	88.8	–	42.9	61.8	61.8	42.9
10 days	82.3	94.3	91.5	–	–	–	100	–	84.6	96.6	–	91.5	–	–	–	87.2	100	100	81.8
11 days	84.6	98.3	100	–	–	–	–	–	94.3	100	–	97.2	–	–	–	88.6	–	–	–
12 days	89.2	100	–	–	–	–	–	–	100	–	–	100	–	88.8	–	89.2	–	–	–
13 days	100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100	–	–	–

TABLE 6

Bromination of Nitrobenzene

Duration of experiment	Quantity of reacted bromine (in %) with catalyst										
	Without catalyst	Mg	Zn	Hg	Al	Pb	Bi	S	Te	I	HBr
30 min.	0	1.7	4.6	1.7	1.2	0.6	6.2	2.3	2.3	0	0.6
9 hrs.	0	1.7	4.6	1.7	1.2	–	6.2	2.3	5.7	–	0.6
1 day	0	3.5	4.6	3.5	1.2	0.6	8	2.9	10.3	0	2.3
3 days	0.6	4	6.2	5.7	3.5	–	9.7	3.5	16.2	0	4
45 days	4	4	8	9.7	6.9	0.6	10.3	13.1	22.2	6.2	4
3 mo.	4	6.9	13.1	11.4	13.1	5.7	13.7	19.9	24.5	8.4	4
11 mo.	5.7	13.1	16	16.2	35.3	9.7	16.2	31.3	27.3	12	5.7

TABLE 7

Yields of Bromobenzene and Dibromobenzene in the Presence of Bromides of Various Elements

Reaction products	Catalysts and their weights (in g)									
	–	$CuBr_2$ 0.44	$ZnBr_3$ 0.45	$AlBr_3$ 0.53	PBr_3 0.86	$AsBr_3$ 0.63	$SbBr_3$ 0.73	S_2Br_2 0.45	IBr_3 0.73	$FeBr_3$ 0.59
C_6H_5Br (in g)	2.27	3.67	14.8	18.65	2.2	3.98	4.94	3.64	9.29	23.51
C_6H_5Br (in %)	7.2	11.6	47.1	56.2	7.1	12.6	15.7	11.5	29.5	74.9
$C_6H_4Br_2$ (in %)	–	–	2.7	–	–	–	–	–	–	3.76

TABLE 8

Effect of Temperature Upon the Benzene Bromination Rate (0.01 g at. wt. Zn per mole of Br_2)

Temp.	Quantity of reacted bromine (in %) for duration of experiment											
	30 min.	2 hrs.	6 hrs.	18 hrs.	2 days	4 days	5 days	6 days	7 days	8 days	10 days	12 days
11-12°	3.8	6.3	10.9	17.2	30	42.3	49	54	59	61	–	62.4
about 18°	3.8	8	15.1	28	46.9	67.8	71.8	76.6	82.5	87	–	100
24-25°	3.8	9.3	24.7	36.8	58.1	75.4	83.2	86.6	92	94	100	–

TABLE 9

Effect of Quantity of Zinc Upon the Benzene Bromination Rate

Quantity of Zn (in g.at.wts. per mole of Br_2)	Amount of reacted bromine (in %) for duration of experiment												
	30 min.	2 hrs.	6 hrs.	18 hrs.	27 hrs.	2 days	4 days	5 days	6 days	7 days	8 days	11 days	12 days	14 days
0.0025	2.6	3.8	6.3	9.7	13.4	19.3	27.2	31.4	33.9	36.4	39.4	44.8	46.9	–
0.005	2.1	4.7	10.5	20.6	28	43.1	65.3	74.9	78.2	85	89.2	95.6	100	–
0.01	3.8	8.0	15.1	28	34.3	46.9	67.8	71.8	76.6	82.5	87.0	95.9	100	–
0.02	2.6	8.0	15.9	28	33.9	44.4	59.2	67	72.4	77.4	84.6	93.3	97.7	–
0.04	6.7	12.2	19.3	30	34.8	44.4	52.3	56.5	59.9	61	67.8	78.7	83.3	–
0.1	2.5	3.8	5.5	12.2	18.9	31	56.5	67.4	72.3	79.1	85	93.3	97.7	100

TABLE 10

Bromination Products of Benzene

Reaction products	Yield of bromination products (in %) with catalyst							
	Without catalyst	Zn	Hg	Bi	Te	H_2O	HBr	CH_3COOH
	22 mo.	25 days	3 mo.	3 mo.	4 mo.	30 mo.	18 mo.	28 mo.
C_6H_5Br	20	100	100	100	100	6	100	10
$C_6H_6Br_6$	80	0	0	0	0	94	Traces	90

TABLE 11

Bromination Products of Toluene

Reaction products	Yield of reaction products (in %) with catalyst							
	Without catalyst	Cu	Mg	Zn	Cd	Hg	Al	Sn	Pb
$BrC_6H_4CH_3$	44	85	43	97	95	56.2	67	86	56.4
$C_6H_5CH_2Br$	56	15	57	3	5	43.8	33	14	43.6

Reaction products	Yield of reaction products (in %) with catalyst							
	Sb	Bi	Te	I	Fe	H_2O	HBr	C_6H_5I	$C_6H_4(NO_2)_2$
$BrC_6H_4CH_3$	84	95.4	95.8	93.4	95.9	Traces	49	54.4	25
$C_6H_5CH_2Br$	16	4.6	4.2	6.6	4.1	100	51	45.6	75

SUMMARY

1. Of the numerous catalysts used in bromination of aromatic compounds, the best have been found to be iron, zinc, birmuth, mercury, cadmium and tellurium. During the reaction process, they are all converted into the corresponding bromides.

2. Zinc in the form of zinc dust can be recommended as a good, practical catalyst for bromination of benzene.

3. The evolution of hydrogen bromide in bromination accelerates further the course of the substitution reaction.

4. Water, acetic acid and aromatic nitro compounds decelerate, or have hardly any accelerating action on the substitution reaction. These compounds, water in particular, also effec the direction of the reaction in such manner that in the bromination of benzene, the content of hexabromocyclohexane is increased, and upon brominating toluene, more benzyl bromide is formed.

5. Upon bromination, catalysis can be homogeneous ($FeBr_3$, $AlBr_3$, HBr) or heterogeneous ($ZnBr_2$).

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INVESTIGATION OF ALLENE HYDROCARBONS

III. OXIDATION OF ALLENE HYDROCARBONS BY ACETYL HYDROGEN PEROXIDE

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The Prilezhaev reaction [1] has been studied in a large number of ethylene series hydrocarbons and their derivatives, but its applicability to the most highly unsaturated hydrocarbons has been given little study.

Prilezhaev studied the oxidation of phenylacetylene by benzoyl hydrogen peroxide [2]. Although the reaction took four months, the oxidation products gave him nothing on which to judge its chemistry. Prilezhaev [3] and Nametkin and Bryusov [4] oxidized the diolefin hydrocarbons, and obtained the mono- and dioxides depending upon the quantity of hydrogen peroxide. Muskat and Herman [5] oxidized cis-1-phenylbutadiene-1,3 with benzoyl hydrogen peroxide in chloroform at 0 and 25°. In the first instance they obtained 1-phenyl-3-benzoyl-oxybuten-1-ol-4 and in the second 1-phenyl-1,3-dibenzoyloxybutanediol-2,4. They isolated small quantities of the monoxide with oxide ring in the 3,4 position, and the dioxide, at the same time as they obtained the benzoyl derivatives.

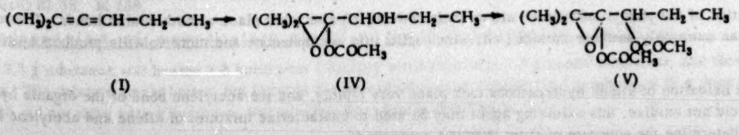
Pummerer and Reindel [6] oxidized the same hydrogen peroxide in chloroethane at 0° with butadiene-1,3 and 2-methylbutadiene-1,3 and got only the monoxide, the second double bond not being affected in their opinion. With 2-methylbutadiene-1,3 the oxide ring was formed in the 1,2 position. Everett and Kon [7] oxidized benzoyl hydrogen peroxide in chloroform with ice-cooled monoxides of butadiene-1,3, 2-methylbutadiene-1,3, hexadiene-2,4, 2,3-dimethylbutadiene-1,3 and 1-phenylbutadiene-1,3. The dioxides were produced in each case. With the two last hydrocarbons, however, the pure dioxides were not isolated. Malenok, Sologub and Kulkina [8] oxidized acetyl hydrogen peroxide with vinylacetylene hydrocarbons and established that oxidation pertained only to the double bond, while the triple bond was titrated out with bromine after the reaction. We [9] oxidized 80-90% acetyl hydrogen peroxide in ether at 25° with 2,4-dimethylhexadiene-2,4, 2,4-dimethyloctadiene-2,4 and 2,4,7-trimethyloctadiene-2,4. In all cases the reaction products were dioxides and monoacetate glycol oxides.

This small group of studies constitutes the whole of the investigation of organic hydrogen peroxide oxidation by diolefin, acetylene and butadiene hydrocarbons. The effect of this oxidizing agent upon allene hydrocarbons has not been studied at all.

The works cited above testify to the lack of uniformity in the relation of organic hydrogen peroxides to various types of bonds. Therefore, study of the oxidation reactions of allene hydrocarbon organic hydrogen peroxides, which are often found with acetylene and butadiene hydrocarbons because of their mutual isomeric conversions, presents undeniable interest as a possible means of analyzing such mixtures. It is also important to find a means of establishing the structure of these hydrocarbon isomers, as the reliable ozonization method of resolving this problem is quite difficult, while the oxidation of acetylene hydrocarbons and their allene isomers with a one per cent permanganate solution is inapplicable for this purpose, as shown by Favorsky and Bon [10], as it gives identical reaction products. Finally, it is of interest to clarify the possibility of producing allene hydrocarbon dioxides, which have not been studied at all. The literature contains but a single example [11], tetraphenylallene dioxide, obtained by oxidizing that hydrocarbon with chromium anhydride.

In the present study, we oxidized 2-methylhexadiene-2,3 (I), 2-methyloctadiene-2,3 (II) and 2-methyl-4-phenylpentadiene-2,3 (III) with acetyl hydrogen peroxide.

Oxidation of hydrocarbon (I) was with 69.8% acetyl hydrogen peroxide in anhydrous ether. The amount of hydrogen peroxide was based on calculation for oxidation of both double bonds. The reaction was energetic and heat-producing, and within an hour virtually all the hydrogen peroxide had been used. A substance with b.p. 83-85°/2 mm, analysis of which corresponded to monoacetate glycol oxide (IV) was isolated from the oxidation products. Its structure probably is that of (IV).



$$(CH_3)_2C{=}C{=}CH{-}CH_2{-}CH_3 \rightarrow (CH_3)_2C{-}\underset{OCOCH_3}{C}{-}CHOH{-}CH_2{-}CH_3 \rightarrow (CH_3)_2C{-}\underset{OCOCH_3}{C}{-}\underset{OCOCH_3}{CH}{-}CH_2{-}CH_3$$

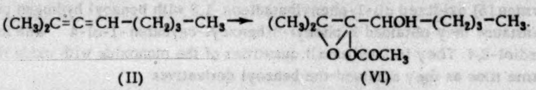
(I) (IV) (V)

Compounds containing the oxide ring with an alcohol or ether group at the carbon atom of the ring, are known in the literature.

The first known substance of similar structure was Butlerov's oxoctenol [12], for which he proposed two equally probable formulas: a hydroxy acid and a keto alcohol. Similar compounds were apparently obtained by Khaletsky [13] and Madelung and Oberwegner [14]. Favorsky [15], Danilov, Venus-Danilova and their pupils [16] accepted the formation of this hydroxy acid as the explanation for certain chemical processes. The work of Temnikova and associates [17] and also that of Stevens and associates [18] is entirely convincing proof of the possible existence of hydroxy acids of the given structure.

When monoacetate glycol oxide (IV) was reacted with acetic anhydride, the result was apparently the diacetate (V). In this reaction the oxide ring was not affected.

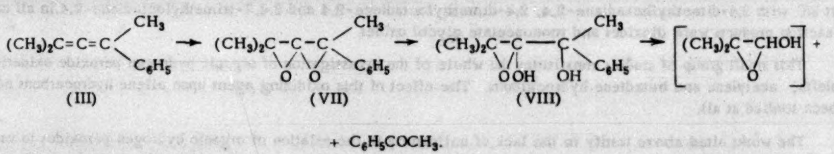
When hydrocarbon (II) was oxidized, the quantity of hydrogen peroxide used in the reaction corresponded to the two double bonds. The reaction products were exceedingly unstable and it did not prove possible to isolate them in pure form. However, the chemical character of the substance separated from the oxidation products and having b.p. 120-123° = 3 mm made it possible to regard it as being monoacetate glycol oxide (VI)



$(CH_3)_2C{=}C{=}CH{-}(CH_2)_3{-}CH_3 \rightarrow (CH_3)_2C{-}C{-}CHOH{-}(CH_2)_3{-}CH_3$ (O bridge; $OCOCH_3$)

(II) (VI)

To obtain 2-methyl-4-phenylpentadiene-2,3 (III) we reacted phenyl magnesium bromide with mesityl oxide. The literature contains contradictory data on this reaction [19]. The 2-methyl-4-phenylpenten-2-ol-4 [20] of which we obtained a yield of up to 75% by this reaction was subjected to dehydration, giving 2-methyl-4-phenylpentadiene-2,3 (III). If the magnesia complex be decomposed by sulfuric acid, without cooling, one obtain no hydrocarbon (III) instead of alcohol. Oxidation of (III) with acetyl hydrogen peroxide was energetic and, as in the previous instances, was virtually complete within 30-40 minutes, while the consumption of hydrogen peroxide corresponded to the oxidation of two double bonds. The oxidation products included substance (VII) with b.p. 129-134°/2.5 mm, of which analysis gave reason to conclude that it was 2-methyl-4-phenyl-dioxido-2,3,3,4-pentane (VII).



(III) (VII) (VIII)

Dioxide (VII) proved unstable, as Prilezhaev [21] had noted of the monoxide; each redistillation produced low-boiling fractions chiefly containing acetophenone and condensation products.

The production of acetophenone during distillation of the oxidation products of 2-methyl-4-phenylpentadiene-2,3 may be explained by the partial hydration of dioxide (VII), with production of glycol oxide (VIII); the latter, like certain pinacols [22], benzalacetone oxide [23], methylisobutenylphenylcarbinol oxide [19] and certain alcohol oxides [24], cleaves on distillation into acetophenone and more volatile products whose formation we failed to expect and therefore did not trap. It must be noted that 2-methyl-4-phenylpentadiene-2,3 (III) is oxidized by atmospheric oxygen upon long storage, and becomes a thick viscous mass. Attempts to distill these oxidation products resulted in violent decomposition, and again in the production of acetophenone.

The presence of acetophenone glycol oxide (VIII) in the decomposition products confirms the structure of hydrocarbon (III), oxidized by us, as 2-methyl-4-phenylpentadiene-2,3, and also indicates that the oxide ring to whose carbon atom the phenyl radical is attached is highly unstable.

Thus, the reaction of acetyl hydrogen peroxide with allene hydrocarbons of the aliphatic series results in oxidation of both double bonds, while the reaction products are monoacetyl derivatives of the glycol oxides (IV and VI). Monoacetyl derivative (IV) and acetic anhydride produce the diacetyl derivative of glycol oxide (V).

Oxidation of the phenyl-substituted allene hydrocarbon (III) also takes place at both double bonds. The reaction product is an extremely unstable dioxide (VII) which splits into acetophenone and more volatile products upon distillation.

As the oxidation of allene hydrocarbons took place very rapidly, and the acetylene bond of the organic hydrogen peroxides did not oxidize, this oxidizing agent may be used to characterize mixtures of allene and acetylene hydrocarbons or to determine the structure of these isomeric compounds.

EXPERIMENTAL

1. Production of 2-Methylhexadiene-2,3.

Bromination of 2-methylhexanol-2 gave 2-methyl-2,3-dibromohexane.
B.p. 79-83°/18 mm, n_D^{20} 1.4992, d_4^{20} 1.497 MR_D 50.51; calculated 50.05.

The dibromide was treated with twice of caustic potash in 33% alcohol solution. The hydrogen bromide was separated by heating the mixture to boiling. After heating for two hours over a boiling water bath the reaction mixture was diluted with water, the precipitated monobromide was separated out, and driven off from the residue with water vapor. The alcohol was with water, and the 2-methyl-3-b mohexene-2 was dried with calcium chloride and distilled. The yield attained 90% of theoretical.

B.p. 82-83° (70 mm), n_D^{20} 1.4700, d_4^{20} 1.1748, MR_D 42.03; calculated 41.95.
0.1912, 0.3301 g sub.; 22.94 g benzene: Δt 0.240, 0.425° Found: :M 178.7, 174. $C_7H_{13}Br$. Calculated: M 177.

The structure of the monobromide was demonstrated by permanganate oxidation. 8 g monobromide was emulsified in 100 ml water and 1000 ml of 1% $KMnO_4$ solution was added gradually as color was lost. After saturation with carbon dioxide and neutralization with potash, the residue was filtered, and the neutral volatile oxidation products were driven off the filtrate. The first 10-15 ml of distillate was processed with semicarbazide. The semicarbazone thus obtained melted at 123.5°. A sample mix of butyraldehyde with the semicarbazone did not result in lowering the melting point. The residue gave additional crystals of semicarbazone, which melted at 180-185°. A sample mixture of acetone with the semicarbazone melted at 181-185°. After the neutral volatile products were separated out, the distillate was acidified with sulfuric acid, and volatile acids were driven off. These products were treated with silver carbonate, and 3 fractions of silver salts were obtained, whose analysis showed the presence of butyric acid.

1st fraction 0.1830 g sub.: 0.1018 g Ag. 2nd fraction 0.1831 g sub.: 0.1018 g Ag. 3rd fraction 0.1496 g sub.: 0.0824 g Ag. Found %: Ag 55.62, 55.59, 55.14. $C_4H_7O_2Ag$. Calculated %: Ag 56.23.

2-Methylhexadiene-2,3 (I) was obtained by heating 100 g 2-methyl-3-bromo-hexene-2 and 200 g alcohol solution of caustic potash (66 g KOH and 134 g ethyl alcohol) in an autoclave for 7 hours at a temperature of 130-135°. The phosphorous bromide derived, which was always 50% of the theoretical, was filtered off; the hydrocarbon was distilled over a water bath to 80°, and the alcohol was washed with water. 520 g monobromide was treated in the same way. After washing with alcohol, the residue, amounting to 145 g, was dried with calcium chloride. Repeated distillation of the residue gave 30 g substance (12.6%).

B.p. 97-100° (748 mm) n_D^{20} 1.4351, d_4^{20} 0.7331, MR_D 34.2; calculated 33.59.
0.2179 g sub.: 0.6962 g CO_2; 0.2452 g H_2O. 0.1718. 0.3512 g sub.; 24.9 g benzene: Δt 0.344, 0.733°. Found %: C 87.13; H 12.59; M 103, 98.8. C_7H_{12}. Calculated %: C 87.50; H 12.50. M 96.

Oxidation of 2-methylhexadiene-2,3 with acetyl hydrogen peroxide

59 g 69.8% acetyl hydrogen peroxide, calculated for oxidation of both double bonds, was added gradually to 25 g hydrocarbon in 70 ml dry ether. The reaction was accompanied by much giving off of heat, so that the reaction mixture was cooled with snow water and the hydrogen peroxide was added slowly to prevent the temperature from rising above 25°. After 24 hours it was determined that 5.1 g unreacted hydrogen peroxide remained. Thereafter it was reduced in quantity very slowly, which could be attriubted to its decomposition. The acetic acid was neutralized by a 10% soda solution, and the ether layer was separated off, washed with water and dried with Na_2SO_4 with a small admixture of K_2CO_3.

Double distillation of the oxidation products isolated 7.6 g of a substance that boiled at 83-85° (2 mm). It dissolved in water and in various other solvents and was rapidly oxidized by permanganate.

n_D^{20} 1.4370, d_4^{20} 1.0181, MR_D 47.90; calculated 46.51.
0.1754, 0.1971 g sub.: 0.3743, 0.4232 g CO_2; 0.1421, 0.1623 g H_2O. 0.1288 g sub.: 16.26 ml CH_4(0°, 760 mm), 0.4383 g sub.: 3.9 ml 0.6 N KOH. 0.1545, 0.3129 g sub.; 25.8 g benzene: Δt 0.174, 0.350°. Found %: C 58.20, 58.55; H 9.00, 9.21; OH 9.64; CH_3COO 31.47. M 176.9, 178.1. $C_9H_{16}O_4$. Calculated %: C 57.50; H 8.50; OH 9.05; CH_3COO 31.38. M 188.

Condensation of monoacetate glycol oxide (IV) by acetic anhydride

3.7 g substance was heated 1.5 hours over a boiling waterbath with 8.5 g acetic anhydride, and then boiled 4 to 5 hours. The mixture turned brown but became almost colorless upon cooling. 2.1 g substance of a thick consistency, which did not show active hydrogen, was isolated after double distillation.

B.p. 123.5-124° (7 mm), n_D^{20} 1.4325, d_4^{20} 1.0447, MR_D 57.16; calculated 55.88.

0.1774, 0.2086 g sub.: 0.3813, 0.4507 g CO_2. 0.1298, 0.1536 g H_2O. 0.4191 g sub.: 39.2 ml 0.1 N NaOH after standing for 24 hours. 0.1508, 0.3359 g sub.; 16.35 g benzene: Δt 0.235, 0.507°. Found %: C 58.70, 58.93; H 8.33, 8.24; CH_3COO 54.6, M 201.7, 208.3. $C_{11}H_{18}O_5$. Calculated %: C 57.39, H 8.20; CH_2COO 51.3. M 230.

II. Production of 2-Methyloctadiene-2,3

Bromination of 2-methyloctanol-2 gave 2-methyl-2,3-dibromoctane.

B.p. 113-116° (13 mm), n_D^{20} 1.4902, d_4^{20} 1.3837, MR_D 59.57; calculated 59.47.

Treatment of the dibromide with alcoholic alkali gave the monobromide — 2-methyl-3-bromoketene-2.

B. p. 112-117° (56 mm), n_D^{20} 1.4660, d_4^{20} 1.0882, MR_D 52.17; calculated 51.23.

0.1734 g sub.: 0.1634 g AgBr. Found %: Br 40.10. $C_9H_{17}Br$. Calculated %: Br 39.03.

2-Methyloctadiene-2,3 was produced by heating 150 g 2-methyl-3-bromoctane-2 and 300 g of an alcohol solution of caustic soda (200 g alcohol and 100 g KOH) for 7 hours in an autoclave at 128-130°. The hydrocarbon was driven off at 112°, dried with calcium chloride and redistilled at 140-145° (744 mm). Yield was 9-10% of theoretical.

n_D^{20} 1.4370, d_4^{20} 0.7570, MR_D 42.90; calculated 41.88.

0.1670 g sub.: 0.5304 g CO_2; 0.1928 g H_2O. 0.1192 g sub: 20.77 g benzene: Δt 0.212°. Found %: C 86.62; H 12.92. M 132.8. C_9H_{16}. Calculated %: C 87.10. H 12.90. M 124.

The substance contained a small amount of displaced halide.

Oxidation of 2-methyloctadiene-2,3 by acetyl hydrogen peroxide.

24 g 81% acetyl hydrogen peroxide was added as it reacted to 22 g hydrocarbon in 44 ml ether at a temperature of not more than 25°. Oxidation was practically complete after 24 hours. The reaction products, treated as in the previous case, were double distilled in a vacuum. They proved to be unstable substances, and we were unsuccessful in isolating them in pure form, as partial decomposition occurred. 3.4 g of substance was separated, which boiled at 120-123° (3 mm), was readily discolored by permanganate and, when dissolved in organic solvents, revealed active hydrogen.

n_D^{20} 1.4415, d_4^{20} 0.9711, MR_D 58.80; calculated 55.75.

0.1955, 0.1468 g sub.: 0.4569, 0.3437 g CO_2; 0.1800, 0.1383 g H_2O. 0.1298 g sub.: 17.67 ml CH_4 (0°, 760 mm). 0.1260 g sub.: 17.4 ml CH_4 (0°, 760 mm). 0.0903, 0.1837 g sub.; 15.85 g benzene: Δt 0.157, 0.292°. Found %: C 63.60, 63.85; H 9.83, 9.83; OH 10.40, 10.34. M 186.8, 204. $C_{11}H_{20}O_4$. Calculated %: C 61.10; H 9.26; OH 7.87. M 216.

III. Production of 2-methyl-4-phenylpentadiene-2,3

600 ml 5% sulfuric acid was added to 150 g 2-methyl-4-phenylpenten-2-ol-4, produced as described previously [20]; the mixture was heated for two hours over a boiling water bath. 135 g of dehydration product was recovered and dried with calcium chloride. The result of triple vacuum distillation was a substance that boiled at 94-99° (9 mm), analysis of which coincided closely with that of 2-methyl-4-phenylpentadiene-2,3.

n_D^{20} 1.5537, d_4^{20} 0.9235, MR_D 54.83; calculated 53.08.

0.1954, 0.1959 g sub.: 0.6442, 0.6483 g CO_2; 0.1531, 0.1608 g H_2O. 0.1870, 0.3323 g sub.; 21.16 g benzene: Δt 0.300, 0.524°. Found %: C 90.35; H 8.77, 9.18. M 151.4, 154.1. $C_{12}H_{14}$. Calculated %: C 91.07; H 8.79, M 158.

Number of double bonds : 0.4533 g sub.: 0.9150 g Br. Found %: Br 66.88. $C_{12}H_{14}Br_4$. Calculated %: Br 66.92.

It must be noted that each redistillation of the hydrocarbon was accompanied by fractions boiling lower and higher, and that it proved impossible to obtain the hydrocarbon within narrower temperature limits.

Oxidation of 2-methyl-4-phenylpentadiene-2,3 by acetyl hydrogen peroxide.

87 g 69.8% acetyl hydrogen peroxide was poured slowly into 60 g hydrocarbon in 100 ml ether at not above 25°. Oxidation was very energetic. The mixture was left overnight in cold water. The next day 6.02 g acetyl hydrogen peroxide was found in the mixture, but only 0.54 g the day after that. The acetic acid was neutralized, first with a 10% soda solution, and then with dry soda. The ether extract was washed with water and dried with sodium sulfate. After the ether was driven off an oily liquid remained which when distilled even in high vacuum (2.5 mm), underwent considerable condensation and liberated acetophenone, which was the major component of the first fractions. Repeated redistillation produced 9.8 g of substance that boiled at 129-134° (2.5 mm). This was an oily yellow liquid,

readily oxidized by permanganate. It constituted a mixture with active hydrogen.

n_D^{20} 1.5210, d_4^{20} 1.0830, MR_D 53.32; calculated 53.16.

0.1932, 0.1878 g sub.: 0.5254, 0.5063 g CO_2; 0.1326, 0.1319 g H_2O. 0.1413 g sub.: 8.96 ml CH_4 (0°, 760 mm). 0.1339, 0.2833 g sub.: 25.8 g benzene: Δt 0.137, 0.287°. Found %: C 74.16, 73.61; H 7.68, 7.68; OH 4.84. M 194.7, 200.1. $C_{12}H_{14}O_2$. Calculated %: C 75.78; H 7.86. M 190. $C_{12}H_{16}O_3$. Calculated %: C 69.20; H 7.69; OH 16.3. M 208.

The substance of the first fractions smelled of acetophenone and distilled at 201.5° at normal pressure. Its semicarbazone had a m.p. of 197° after recrystallization. A sample mixed with acetophenone semicarbazone showed no reduction in melting ponit.

SUMMARY

1. Three allene hydrocarbons — 2-methylhexadiene-2,3 (I), 2-methyloctadiene-2,3 (II) and 2-methyl-4-phenylpentadiene-2,3 (III) were subjected to oxidation by acetyl hydrogen peroxide.

2. Oxidation of allene hydrocarbons by acetyl hydrogen peroxide takes place at both double bonds, with the formation of monoacetyl derivatives of the glycol oxides with hydrocarbons (I) and (II), and of an unstable dioxide in the case of hydrocarbon (III).

3. Oxidation with acetyl hydrogen peroxide may apparently serve as a means of analyzing mixtures of allenes with their acetylene hydrocarbon isomers.

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1) See C. B. Translation, page a-151.
2) " " " " page a-383.
3) " " " " page 1197.
4) " " " " page 1401.
5) " " " " page 1567.
6) " " " " page 1437.
7) " " " " page a-197.
8) " " " " page 231.

CONJUGATED ADDITION REACTIONS OF HALOGENS TO OLEFINS. I.

A. I. Titov and F. L. Maklyaev

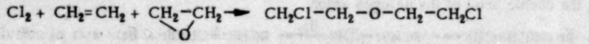
The concept of conjugated reactions, developed by Shilov [1], has been assuming greater and greater significance.

By a conjugated reaction of halogens, the authors understand this to mean reactions in which a third component is involved in the interaction of halogens with olefins, wherein, however, the third component does not react by itself with the multiple bond under such conditions.

As an example of such reaction can be given the side formation of β-bromoethyl nitrate during the interaction of ethylene with bromine in potassium nitrate [2],

$$Br_2 + CH_2{=}CH_2 + KNO_3 \rightarrow BrCH_2{-}CH_2{-}ONO_2 + KBr, \qquad (1)$$

or the synthesis of chlorohydrins when passing olefins and chlorine into water [3,4], the synthesis of halogenated esters [5-18], the original chlorex method of Arbuzov [19],



$$Cl_2 + CH_2{=}CH_2 + \underbrace{CH_2{-}CH_2}_{O} \rightarrow CH_2Cl{-}CH_2{-}O{-}CH_2{-}CH_2Cl \qquad (2)$$

or the appearance of halogenated β-lactones by reaction of bromine with dimethylfumaric and with maleic acids [20].

In the authors' opinion, a majority of the addition reactions of halogens and of halogenating agents, of both ionic and radical character, to olefins can, under suitable conditions, become conjugated. In this series of works, however, the authors have considered only reactions of the ionic type.

To explain the involvement of a third component in the reaction of halogens with olefins, Gomberg [4], Ushakov [9], Conant [13], and Birckenbach [16] postulate that the first stage is an interaction of halogen with the third component, and the second – addition of this intermediate product to the olefin, for example:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl,\ HOCl + CH_2{=}CH_2 \rightarrow HOCH_2{-}CH_2Cl. \qquad (3)$$

Shilov presented [22] convincing kinetic proofs of the inaccuracy of the above-postulated scheme. Such point of view is not at all applicable to an explanation of the involvement of sulfuric acid in the reaction (see further on), which was discovered by the authors, because in such a case the following unlikely reaction would need to be adopted:

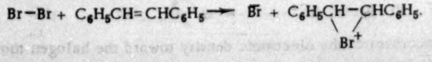
$$Cl_2 + H_2SO_4 \rightarrow ClOSO_3H + HCl. \qquad (4)$$

In addition, such reaction does not explain the formation of a trans-addition product.

Francis [2], Ingold, and others, postulate that the initial reaction phase consists of carbonium-ion formation:

$$Br \leftarrow Br + CH_2{=}CH_2 \rightarrow Br^- + BrCH_2{-}\overset{+}{C}H_2 \xrightarrow{Cl^-} BrCH_2{-}CH_2Cl, \qquad (5)$$

which reacts further with other particles, for example the chloride ion, according to Equation (5). Interaction of the same carbonium-ion in the second stage with bromide ion leads to formation of the usual reaction product – 1,2-dibromoethane. Objection to the appearance of a carbonium-ion in the case of purely aliphatic olefins should be made on the basis of energy principles [24]. The Ingold hypothesis is also negated by formation of various stereoisomeric halogen addition products to cis- and trans- isomers, because, according to such a concept, the latter would be obliged to produce as an intermediate one and the same cation, and hence, one and the same mixture of products. To make the Ingold interpretation agree with stereochemical data, Tarbell and Bartlett [25] consider that the second reaction phase proceeds very rapidly, and that the cations produced do not have time to assume one and the same planar configuration. With this thought in mind, Roberts and Kimball [26] postulate that the intermediate cation formed possesses an onium three-membered structure

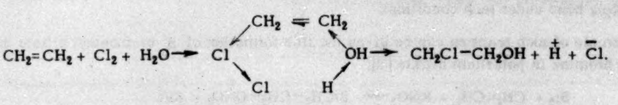


$$Br{-}Br + C_6H_5CH{=}CHC_6H_5 \rightarrow \bar{Br} + \underbrace{C_6H_5CH{-}CHC_6H_5}_{Br^+}. \qquad (6)$$

Thanks to cyclization variance in configuration is preserved, and the subsequent interaction, for example with bromide ion, accompanied by Walden inversion, leads to various trans-addition products. The viewpoint of Dewar [39] coincides with this hypothesis.

The Tarbell and Bartlett proposal does not eliminate the energy contradictions for reaction with purely aliphatic olefins, particularly for ethylene itself. In cases of halogen additions to cis- and trans-stilbenes, where the cation could have been sufficiently stable, formation of different products was nonetheless observed. The Roberts and Kimball hypothesis, despite instability of a three-membered ring, might apparently have been considered probable for iodine, and partially so for the bromine addition, but the formation of such onium compounds with chlorine or fluorine is improbable.

Shilov [21, 22], with his coworkers, in extensive investigations of the kinetics of formation of ethylene chlorohydrin used the following scheme for presentation of the reaction mechanism, indicating by arrows the direction of migration of electrons:



$$CH_2{=}CH_2 + Cl_2 + H_2O \rightarrow \begin{array}{c} CH_2 \rightleftharpoons CH_2 \\ Cl \qquad\qquad OH \\ Cl \qquad\qquad H \end{array} \rightarrow CH_2Cl{-}CH_2OH + \overset{+}{H} + \overset{-}{Cl}. \qquad (7)$$

Similar schemes are to be found in the works of Hennion [17], Irwin [27], and other authors.

To explain variation in reaction products for cis- and trans-olefins, Ogg [28, 29, 30] advanced a hypothesis of primary addition along the double bond of the halogen anion

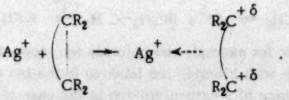
$$\overline{Br} + RCH{=}CHR \rightarrow RCHBr{-}\overline{C}HR \xrightarrow{Br_2} RCHBr{-}CHRBr + \overline{Br}. \qquad (8)$$

Acceptance of anion addition to nucleophilic olefins contradicts all chemical experience, however.

In 1946, the authors approached an understanding of the nature of conjugated addition reactions, and found new fields for application on the basis of the following concepts of the chemical nature of olefins and halogens.

Olefins are clearly defined, and effectively nucleophilic. This tendency, for example, is exemplified by their ability to give immediate coloration with tetranitromethane, as well as with standard bases, and to dissolve hydrogen fluoride and sulfur dioxide, apparently with formation of salt-like solvates. They enter into complex formation with numerous metallic halides of the aluminum chloride type, hydrogen bromide [31], and the like. In some olefins the basic properties are displayed so strongly that they are able to displace aniline from its hydrochloride, and even ammonia from ammonium chloride [32].

It has been considered that the carriers of the basic (electron donating) olefins are to be found in the π-bond. As is known, electrons of the π-bond are asymmetrically distributed with reference to the common axis of the carbon atoms (in other words, the G-bond), because of which they are mobile and stericly accessible to the action of electrophilic centers of other particles. These peculiarities of the π-bond we shall express by formulas of the type $R_2C\overset{\frown}{-}CR_2$, in which the π-electrons are designated by the arc; to simplify the outline, the usual schemes $R_2C{=}CR_2$ can be used, keeping in mind, however, their original context. From the above-stated point of view, complex formation of olefins, for example with Ag^+, can be expressed by the following equation, wherein the embedding of π-electrons into the cation sphere is indicated by the symbol $\dashrightarrow$



$$Ag^+ + \left(\begin{array}{c} CR_2 \\ \vert \\ CR_2 \end{array} \right. \rightarrow Ag^+ \dashleftarrow \left(\begin{array}{c} R_2C^{+\delta} \\ \\ R_2C^{+\delta} \end{array} \right. . \qquad (9)$$

Such understanding of this process is confirmed by the decrease in combination frequencies of double bonds in the complex, due to deformation of the π-electron orbit.

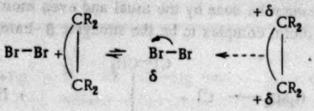
In their chemical behavior, halogens display an active electrophilic behavior; they can, with adequate justification, be related to the aprotonic acids as interpreted by Lewis [33, 34] and Usanovich [35]. The effective acidity of the halogens is evident from their ability to react rapidly with alkalies, amines, thioesters and many anions,

$$R_3N + Br{-}Br \rightleftharpoons R_3N \dashrightarrow Br\overset{\curvearrowright}{-}Br, \qquad (10)$$

$$\overline{Br} + Br{-}Br \rightleftharpoons \overline{Br} \dashrightarrow Br\overset{\curvearrowright}{-}Br. \qquad (11)$$

The arrow is this formula indicates displacement of the electronic density toward the halogen molecule, and the attendant possibility for strengthening the halide ion – up to the point of rupture – as happens to some degree in complexes with amines and amides.

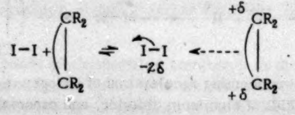
Comparison of such data on the chemical nature of olefins and halogens leads to the conclusion that interaction between them is perhaps of an acid-base character



(12)

This conclusion is strengthened by formation of molecular compounds of bromine with tetraarylethylenes [36]. The complexes are stable only upon cooling, and are dissociated at normal temperature. The complex formation and dissociation processes do not change the configurations of cis- and trans- isomers, in agreement with preservation of the double bond in the complex as adopted by the authors.

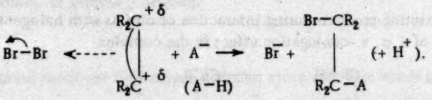
The most spectacular proof of existence of an acid-base interaction of halogens with olefins is the appearance of a brownish color, and a dipole moment (1.5 D) for the iodine in a solution of diisobutylene [37], which can be explained by formation of the complex:



(13)

With iodine solution in saturated hydrocarbons, no increased polarization was found, nor was a dipole moment therefor found. In this sense, iodine behaves similarly to some other aprotonic acids. We might mention that iodine catalyzes many reactions which are accelerated by acids.

Carbon atoms of the complex (Equation 12) should be highly electrophilic, with steric accessibility for interaction from the side opposite to the halogen molecule. This permits, in accordance with the general theory of alkylating agents [40], one to consider ready interaction of the complex (Equation 12) with anions, A^-, or their donors (A−H), with the formation of addition products of olefin and halogen atom and grouping A in the trans-position:

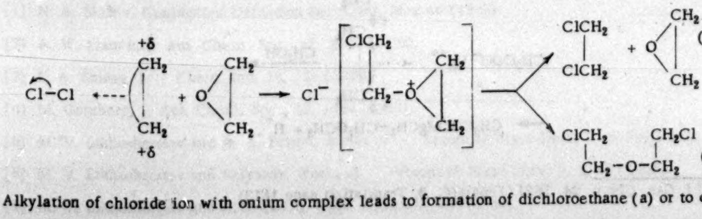


(14)

A combination of Equations (12) and (14) represents, in the authors' opinion, the mechanism of conjugated addition reactions of halogen with involvement of the third component − the anion, or its donor.

If A^- be considered the halogen anion, or H−A a molecule of hydrogen halide, then a combination of Equations (12) and (14) will express the addition mechanism of the halogens themselves in accordance with the ionic complex type. In conformity with this fact, Shilov [21] demonstrated that side reaction formation of dichloroethane during synthesis of ethylenechlorohydrin proceeds in proportion to the concentration of chloride ion; an analogous effect of concentration of halide ion and hydrogen halide has been observed in coupling reactions of the same type. An increase in the reaction rate of bromine with ethylene by 50-130-fold with decrease of temperature from 25 to 0° [38] is found to be in accordance with the assumption of complex formation role; the accelerating action of small amounts of added water upon this reaction, and the effect of polarity of the reactor walls, also confirm this hypothesis.

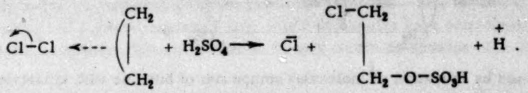
By schemes analogous to (14), the course of more complex conjugated reactions of halogens with olefins can be presented. For example, synthesis of chlorex according to Equation (2) occurs, in the authors' opinion, through the appearance of an onium complex:



(15)

Alkylation of chloride ion with onium complex leads to formation of dichloroethane (a) or to chlorex (b).

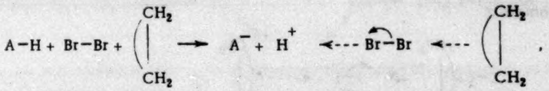
The authors have demonstrated for the first time that a mixture of halogen and olefin is able, under appropriate conditions, not only to alkylate electrodonating molecules and salts, but also very strong, free acids,• themselves, sulfuric, benzene, and chlorosulfonic, which cannot be done by the usual and even most vigorous alkylating means. This makes it possible to consider halogen with olefin complex to be the strongest β-halogenalkylating agent available.



$$\overset{\frown}{\text{Cl}}-\text{Cl} \dashleftarrow \left(\begin{matrix}\text{CH}_2\\ \|\\ \text{CH}_2\end{matrix}\right) + \text{H}_2\text{SO}_4 \longrightarrow \bar{\text{Cl}} + \begin{matrix}\text{Cl}-\text{CH}_2\\ |\\ \text{CH}_2-\text{O}-\text{SO}_3\text{H}\end{matrix} + \overset{+}{\text{H}}\,. \qquad (16)$$

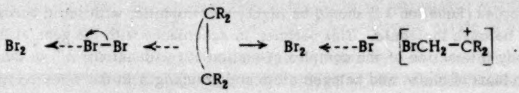
By the method of conjugated reaction — by simultaneous introduction of halogen and olefin to anhydrous acids — it was possible to achieve in good yields the synthesis of β-haloalkyl esters of many different acids.

It is quite possible that in these reactions the strong acids, A — H, promote formation of a complex of type (12) by means of increased polarization of the halogen molecule,



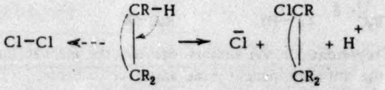
$$\text{A}-\text{H} + \text{Br}-\text{Br} + \left(\begin{matrix}\text{CH}_2\\ \|\\ \text{CH}_2\end{matrix}\right) \longrightarrow \bar{\text{A}} + \overset{+}{\text{H}} \dashleftarrow \overset{\frown}{\text{Br}}-\text{Br} \dashleftarrow \left(\begin{matrix}\text{CH}_2\\ \|\\ \text{CH}_2\end{matrix}\right), \qquad (17)$$

which is confirmed by the authors' observations concerning acceleration of halogenation of benzene with bromine water upon addition of sulfuric acid. Aprotonic acids of aluminum chloride, and especially the silver and mercury cations, can play an analogous role in activation of halogen. Halogen excess should also act in similar manner, which at times may lead to the appearance of salt-like perhalides [41] under conditions favorable for coupling of the cationoid carbon atoms with R radicals.



$$\text{Br}_2 \dashleftarrow \overset{\frown}{\text{Br}}-\text{Br} \dashleftarrow \left(\begin{matrix}\text{CR}_2\\ \|\\ \text{CR}_2\end{matrix}\right) \longrightarrow \text{Br}_2 \dashleftarrow \bar{\text{Br}}\left[\text{BrCH}_2-\overset{+}{\text{C}}\text{R}_2\right]. \qquad (18)$$

The formation of substitution products during interaction of olefins with halogens takes place, in the authors' opinion, because of the display of a σ, π-conjugation effect in the complex

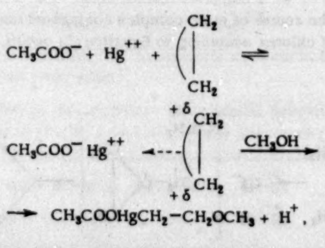


$$\text{Cl}-\text{Cl} \dashleftarrow \left(\begin{matrix}\text{CR}-\text{H}\\ \|\\ \text{CR}_2\end{matrix}\right) \longrightarrow \bar{\text{Cl}} + \left(\begin{matrix}\text{ClCR}\\ \|\\ \text{CR}_2\end{matrix}\right) + \overset{+}{\text{H}} \qquad (19)$$

Substitution becomes unusual in the case of considerable stabilization of the π-bond, as for example, with aromatic rings.

It is expedient to examine a great number of other reactions of unsaturated compounds with electrophilic reagents from the point of view developed above. As the simplest example of processes of the type the formation of methoxyethylmercury acetate by interaction of ethylene with mercury acetate in methanol [42], bringing the latter into reaction

$$(\text{CH}_3\text{COO})_2\text{Hg} \rightleftharpoons 2\text{CH}_3\text{COO}^- + \text{Hg}^{++}$$

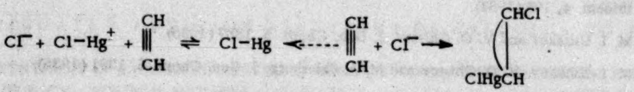


$$\text{CH}_3\text{COO}^- + \text{Hg}^{++} + \left(\begin{matrix}\text{CH}_2\\ \|\\ \text{CH}_2\end{matrix}\right) \rightleftharpoons$$

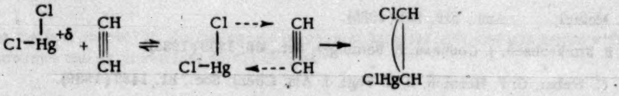
$$\text{CH}_3\text{COO}^-\,\text{Hg}^{++} \dashleftarrow \left(\begin{matrix}{}^{+\delta}\text{CH}_2\\ \|\\ {}_{+\delta}\text{CH}_2\end{matrix}\right) \xrightarrow{\text{CH}_3\text{OH}} \qquad (20)$$

$$\longrightarrow \text{CH}_3\text{COOHgCH}_2-\text{CH}_2\text{OCH}_3 + \text{H}^+,$$

• See article II [J. Gen. Chem. 24, 1631 (1954)] (C. B. Translation page 1613) is similar to the interaction of halogens with olefins in alcoholic medium. In this respect Nesmeyanov [43] and coworkers demonstrated that addition of mercuric chloride to acetylene under the usual conditions proceeds in the trans-position.

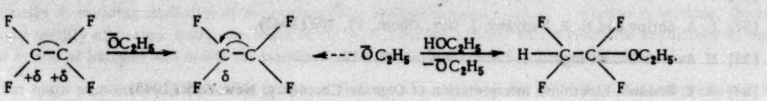

(21)

In the gaseous phase, when interaction cannot go according to the conjugated type of reaction, there results cis-isomers [44], i.e., direct addition actually occurs


(22)

Evidently, addition in the cis-position, though hindered somewhat, is not excluded as a type of interaction with halogens.

Addition along multiple bonds of electrophilic compounds in the presence of bases no doubt also proceeds according to a conjugated type of reaction, for example in the case of hydroxylamine addition to mesityl oxide, or the addition of alcohol to tetrafluoroethylene in the presence of alcoholate [45].


(23)

The difference consists in the fact that because of electron attraction of the negative substituents (CO, F, etc), the unsaturated compounds become the acceptor of electrons of the second component (H_2NOH, $C_2H_5O^-$), and the third component plays the role of donor of protons (C_2H_5OH).

SUMMARY

1. The concept of conjugated reactions for halogen addition along multiple bonds has been introduced, and a review presented.

2. It has been demonstrated that halogen molecules display properties of a strong aprotonic acid (effective electrophilia), and olefins in somewhat less effective manner, possess a basic character due to the relatively weakly-bound π-electrons.

3. It has been accepted that the initial phase of halogen reaction with olefins is the reverse of complex formation of acid-base nature (Equation 12).

Carbon atoms in such a complex possess high effective electrophilic character, and steric accessibility in the trans-position to halogen, thanks to which fact the complex can serve as a most potent β-halogenalkylating material, able to alkylate even the strongest acids (Equation 14).

4. From the point of view developed, the general mechanism, and special cases of halogen interaction with unsaturated compounds according to an ionic mechanism, have been defined.

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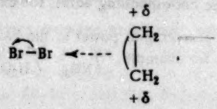
CONJUGATED ADDITION REACTIONS OF HALOGENS TO OLEFINS

II. SYNTHESIS OF β-HALOETHYLESTERS OF BENZENE- AND p-TOLUENESULFONIC ACIDS AND OF β-CHLOROETHYL SULFATES, CHLOROSULFONATE, PHOSPHATE AND MIXED 1,2-DIHALOETHANES

A. I. Titov and F. L. Maklyaev

According to the first article [1] the conjugated reaction of halogens with ethylene begins with formation of a complex, whose structure can be represented by the formula



$$\overset{\frown}{Br}-Br \dashleftarrow \left(\begin{array}{c} +\delta \\ CH_2 \\ | \\ CH_2 \\ +\delta \end{array} \right. \qquad (1)$$

in which the dotted arrow indicates embedding of the π-electrons into the electrophilic halogen atom.

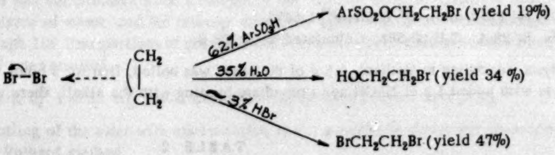
Thanks to steric accessibility of the electrophilic carbons in trans-position relative to bromine, the complex is very readily alkylated, being the donor of the β-bromoethyl cation. This allows wide application of the simultaneous action of halogen and olefin for introducing β-haloalkyl groups into various molecules.

The main purpose of the present work was to find synthetic methods for preparing β-haloethyl esters of sulfonic acids according to the method of conjugated reaction, by directing the alkylating action of the complex upon a third component present. For this purpose, the action of ethylene and bromine upon benzenesulfonic acid salt solution was first tried out

$$Br_2 + CH_2{=}CH_2 + C_6H_5SO_3^- \longrightarrow Br^- + C_6H_5SO_2OCH_2CH_2Br. \qquad (2)$$

The yield of ester, of course, increased with increasing concentration of salt, but even in a saturated solution of potassium benzenesulfonate it only slightly exceeded 10%.

In addition, the authors were able successfully to, replace the salts by the free acids. The sulfonic acids water and hydrogen bromide liberated during the course of reaction were subject to the acylating action of the complex, leading, respectively to the production of ethylenebromohydrin, dibromoethane, and β-bromoethylsulfonate. The relationships observed can be illustrated by the data of one experiment on a conjugated reaction course in p-toluenesulfonic acid solution, combined in Scheme (3).



ArSO$_2$OCH$_2$CH$_2$Br (yield 19%)
62% ArSO$_3$H
CH$_2$
Br—Br
CH$_2$
35% H$_2$O
HOCH$_2$CH$_2$Br (yield 34 %)
3% HBr
BrCH$_2$CH$_2$Br (yield 47%)

(3)

The ratio of reaction product yield to molar concentration of corresponding alkylate component can be called the activity coefficient for this reaction. If the activity coefficient for water (f_{H_2O}) is taken to be unity, then for the above-indicated case

$$f_{H_2O} : f_{ArSO_3H} : f_{HBr} \sim 1 : 3.2 : 700. \qquad (4)$$

One should conclude from the ratio (4) an extremely high activity for hydrogen bromide, or bromide ion, respectively, in the conjugated reactions. With low hydrogen bromide concentrations, and other conditions the same, yield of dibromoethane is increased in almost direct proportion to the analytical content of hydrogen bromide, and the yields of ester and of ethylene bromohydrin are respectively decreased, as can be seen from the experimental data with 64 % p-toluenesulfonic acid solution (Table 2). The activity of hydrogen chloride, or of chloride ion, respectively was 10-15 times less, as from the authors experiments on synthesis of chlorobromoethane and of β-chloroethylbenzenesulfonate, according to the conjugated reaction method.

A comparison of all these results makes possible the deduction that for optimal course of conjugated reaction of ethylene with halogen in sulfonic acid solution in the direction of β-haloethylsulfonate formation, it is necessary: 1) to use anhydrous sulfonic acids as far as possible, 2) to use chlorine as the halogen, 3) to facilitate removal of hydrogen chloride. In fact, yield of β-chloroethylbenzenesulfonate was up to 80% upon interacting ethylene with chlorine in anhydrous benzenesulfonic acid melt at 60° under the condition of bathing the entire surface of the reactor with melt. It is possible that a portion of the dichloroethane formed during this time is due to intramolecular regrouping of the complex by reaction not in contact with the sulfonic acid melt, and possibly some other process, for example:

$$C_6H_5SO_3CH_2CH_2Cl + HCl \rightarrow C_6H_5SO_3H + ClCH_2CH_2Cl.$$

The conjugated reaction of ethylene and chlorine in concentrated sulfuric acid makes possible a good yield of di-(β-chloroethyl)-sulfate (via the acid ester formation stage). Reaction in chlorosulfonic acid leads to formation of β-chloroethylchlorosulfonate, and in phosphoric acid, to tri-(β-chloroethyl)-phosphate.

Let us consider the question of activity of three components in the reactions described. No doubt the activity of the anions and of the salts is greater than of the corresponding acids, for example $f_{SO_4''} > f_{HSO_4'} > f_{H_2SO_4}$. As a first approximation, it can be looked upon as a proportional power of the basic properties of the particle, or, as an inverse proportional power of the acid properties, for example, $f_{NH_3} > f_{H_2O} > f_{CH_3COOH} > f_{CCl_3COOH}$ or $f_{OH'} > f_{CH_3COO'} > f_{CCl_3COO'}$.

A number of other factors, however — polarizability, dimerization, formation of stable solvates, steric factors, structural peculiarities — can, at times, change the indicated order of activities. Thus, the almost insignificant activity of fluoride ion, despite the considerable weakness of hydrofluoric acid in aqueous solution, should be related to the low polarizability of F^- as compared with other halide ions and the stability of its hydrates, of the type $F^- \dashrightarrow H-\overset{-\delta}{O}-H$. The alkylating action upon such hydrates is apparently directed basically to the oxygen.

EXPERIMENTAL

1. Bromoethylation of Potassium Benzenesulfonate. A mixture of 500 g of 50% salt solution and 10.5 ml of bromine was saturated with ethylene with shaker agitation. The addition of bromine, and saturation with ethylene, was repeated. The oily reaction product was washed with water and dried with magnesium sulfate. There resulted the fractions: 25.9 g (33%) of dibromoethane, and 11.2 g (11%) of β-bromoethylbenzenesulfonate with b.p. 198-200° (15 mm).

2. Bromoethylation of Benzene- and p-Toluenesulfonic Acids in Aqueous Solutions. 400 g of a 60 % solution of p-toluenesulfonic acid in mixture with 10.5 ml of bromine was saturated with ethylene with vigorous stirring. The addition of bromine, and the saturation with ethylene, were repeated. The reaction mixture was then diluted with 600 g of water the oily reaction product dried, and then fractionated. 35 g (46%) of dibromoethane and 24 g (21.5%) of β-bromoethyl-p-toluenesulfonate resulted.

B.p. 173-174° (2-3 mm), d_4^{20} 1.531, n_D^{20} 1.5472.
Found %: Br 28.4. $C_9H_{11}O_3SBr$. Calculated %: Br 28.6.

For analysis, according to Volhard, 0.5 g of the ester was boiled, first for 3 hours with 50 ml of water, and then for the same time with added 1 g of NaOH and immediate heating with the alkali, there was formed at once vinyl bromide.

TABLE 1

Experiment No.	Water (in g)	Yield (in %)	
		Ester	Dibromoethane
1	108	19	46
2	408	13	28
3	1608	6	14

TABLE 2

Experiment No.	Sulfonic acid solution (in g)	HBr (average)(in %)	Yield (in %)	
			Ester	Dibromoethane
1	600	1.8	29	33
2	400	2.2	22	45
3	200	3.2	14	63

With increasing amounts of water taken for reaction with 192 g of sulfonic acid, the amount of ethylene bromohydrin was increased, and the yields of ester and dibromoethane decreased (see Table 1).

Upon saturating the sulfonic acid solution of composition corresponding to Experiment 1 of Table 1 with 20 g of hydrogen bromide, the yield of ester was decreased two-fold (9.1%), and the yield of dibromoethane increased to 64%. The effect of hydrogen bromide concentration can also be seen from the following series of experiments with varied amounts of 64% solution of p-toluenesulfonic acid (Table 2).

No noticeable variations in the reaction course were observed in light and in the dark. In experiments with gradual introduction of bromine, the yield of ester was increased somewhat. Upon carrying out the reaction in alcohol, side formation of ethyl-p-toluenesulfonate was observed, due to appearance of esterification.

3. Chloroethylation of Benzenesulfonic Acid. Reaction of ethylene with chlorine in a solution or melt of benzenesulfonic acid was carried out in a cylindrical glass reactor with round bottom. Tubes for chlorine, ethylene, and the outgoing gases were attached by ground-glass joints, as well as the stirrer with a liquid seal of β-chloroethylbenzene sulfonate. Gas feed from the gasometer was regulated by rheometers, the gasometer for chlorine being filled with sodium chloride or calcium chloride solution. The outgoing gases were metered into a trap with reflux condenser, washed with water, and collected in the gasometer. Heating was carried out on a water bath with automatic thermoregulator. Vigorous stirring ensured bathing of reactor top with the reaction mixture.

Pure benzenesulfonic acid was prepared as follows: the benzenesulfonyl chloride was heated for 1 hour under reflux with half the amount of alcohol, and the same volume of water then gradually added and heating continued on the water bath to disappearance of oily droplets of ester. Alcohol and water were distilled off at 20 mm up to 92% content of benzenesulfonic acid (m.p. 50-55°), and then at 2-3 mm at about 150°, 96-98% of product resulting.

456 g of melted 96% benzenesulfonic acid (2.75 moles) was charged into the reactor (700 ml capacity) and at a bath temperature of 60°, with vigorous stirring, 19.6 liters of chlorine (0.87 mole) passed through over a period of 2 hours, and 25 liters of ethylene (1.03 moles); about 8 liters of outgoing gases with 55% water content was collected. Increase in weight of reaction mixture was 61 g. It was diluted with magnesium sulfate, with added magnesium oxide to bind acid radicals. After distilling off the dichloroethane at 150-154° (4 mm), the β-chloroethylbenzene sulfonate was distilled off. Ester yield was 124.7 g (77% of theory based on total reaction products, or 65% according to chlorine) and dichloroethane was isolated in the amount of 16.3 g (23 and 19% respectively).

d_4^{20} 1.352, n_D^{20} 1.530 [2].
Found %: Cl 16.0. $C_8H_9O_3SCl$. Calculated %: Cl 16.1.

Upon passing 5 mole portions of chlorine and ethylene through, there resulted more than 500 g of the ester. When aqueous acid was used, the yield was decreased, but to a lesser extent than in experiments with bromine, due to the lower activity of chloride ion; thus, for a 60% solution, the ester yield was about 30%, dichloroethane 20%, and ethylene chlorohydrin 40%.

4. Chloroethylation of Sulfuric, Chlorosulfonic and Phosphoric Acids.

a) 224 g of sulfuric acid (d 1.84) was poured into the reactor (150 ml capacity) and under the conditions indicated earlier, it was saturated with ethylene and chlorine at a gas rate of 150 ml per minute.

Passage of gases was discontinued when a sample of the reaction mixture remained about $^9/_{10}$ insoluble upon mixing with an equal volume of water, and the relative content of sulfuric acid in it corresponded to about 5%, which necessitated passing through 100 liter portions of chlorine and ethylene. After the above-described treatment and fractionation, about 150 g of ester resulted:

B.p. 143° (3 mm), d_4^{20} 1.4838, n_D^{20} 1.463, corresponding to the literature data [3,4].

After 6 hours boiling of the ester with excess water, it was possible to titrate the theoretical amount of chloride ion according to the Volhard method.

b) 125 ml of chlorosulfonic acid was poured into the reaction mixture, and with ice cooling, over a period of 20 minutes, 4 liters of ethylene and 5 liters of chlorine passed through. Everything was then poured onto ice and extracted with ether. From the dried extract, a fraction, b.p. about 90° (16 mm), was isolated with properties described for β-chloroethylchlorosulfonate [5].

c) Reaction in Phosphoric Acid Carried Out at Normal Temperature. In order to obtain the ester intermediate, it was necessary to pass through a considerable excess of chlorine and ethylene. After treatment similar to that described above, there resulted trichlorotriethylphosphate:

B.p. 180-182° (3 mm), d_4^{20} 1.422, n_D^{20} 1.475 [6,7].

5. Bromoethylation of Sodium Chloride and Hydrogen Chloride. A mixture of 750 ml of 25% sodium chloride solution and 32 g of bromine was saturated in the shaker with ethylene. After washing and drying, the organic layer

was distilled in a dephlegmator. The following fractions were obtained: 1st – 108-112°, 9.4 g; 2nd – 112-116°, 5.0 g; 3rd – 126-130°, 1.8 g. These data made it possible to consider that the content of chlorobromoethane in the reaction product amounted to about 70-80%. Colorless crystals, m.p. 104-107°, resulted from the residue in the flask after extraction with ether and purification with charcoal, which was not investigated further.

Reaction in 150 ml of hydrochloric acid was carried out in a reactor of 200 ml capacity. Bromine was introduced through a dropping funnel with tube reaching to the bottom. With stirrer in operation, and an ethylene passage rate of 200 ml/minute, the addition of bromine at normal temperature was carried out in such manner that its color was not noticeable in the solution. After diluting the reaction mixture with water, and further standard treatment, the following fractions resulted: 1st – 106-112°, 23 g; 2nd – 112-126°, 9.6 g; 3rd – 126-134°, 8.4 g. The residue of 4.7 g was not investigated further. The content of chlorobromoethane in reaction product amounted to about 65%.

Attempt at synthesis of fluorobromoethane was unsuccessful. Interaction of bromine and ethylene in potassium fluoride solution led, on the whole, to formation of ethylene bromohydrin and in the case of hydrofluoric acid, to dibromoethane, while fluorobromoethane could be detected only qualitatively through reactions for the fluoride ion after heating the first distillate with sodium in toluene in a sealed tube at 100°.

SUMMARY

1. Under suitable conditions, a mixture of halogen and ethylene can serve as a vigorous means of β-haloethylation, which action in the solution is distributed over all suitable molecules and anions in proportion to the product of activity and concentration of each of these particles.

2. It has been found that better yields of β-bromo- and β-chloroethyl esters of benzene- and p-toluenesulfonic acids (up to 80%) can be attained when the conjugated reaction of chlorine and ethylene is carried out in melts of anhydrous sulfonic acids under conditions which promote removal of hydrogen chloride and dichloroethane, and keeping to a minimum the interaction on unbathed reactor walls.

3. According to the method of conjugated reaction synthesis di-(β-chloroethyl)-sulfate, β-chloroethylchlorosulfonate, tri-(β-chloroethyl)-phosphate, chlorobromoethane and fluorobromoethane formations have been qualitatively demonstrated.

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INVESTIGATION IN THE FIELD OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XV. REACTION OF METALLIC SODIUM WITH 1,4-DIBROMOCYCLOHEXENE-2

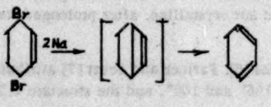
N. A. Domnin and A. S. Beletskaya

In 1903, Zelinsky and Nametkin [1] observed that in the reaction of metallic sodium with a mixture of cis-trans-1,4-dibromocyclohexanes, there was formed dicyclo-(2,0,2)-hexane along with the mixture of products having the composition C_6H_{10}.

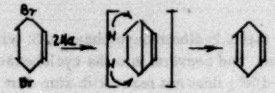
Later, Zelinsky and Kocheshkov [2] demonstrated that in the reaction of metallic sodium with trans-1,4-dibromocyclohexane in anhydrous amyl ether, there is formed the cyclohexadiene-1,3 and diallyl, and with cis-1,4-dibromocyclohexane, the dicyclo-(2,0,2)-hexane is formed.

Although it was not consistently and convincingly proved in either investigation that dicyclo-(2,0,2)-hexane can exist, nevertheless, it is of very great interest, inasmuch as it pertains to the solution of an important stereochemical problem, namely, the ability of a very strongly deformed, and the simplest of dicyclic systems, to exist.

In light of these investigation results, the authors considered it of interest to study these reactions which take place during interaction of metallic sodium with 1,4-dibromocyclohexene-2. It might be expected that interaction would go according to one of the following systems:



(I)



(II)

According to Scheme (I), in time, the dicyclo-(2,0,2)-hexene-2 appearing by rearrangement of the double and the bridge bonds, converts to the conjugated system, cyclohexadiene-1,3. According to Scheme (II), in time, the dicyclo-(2,0,2)-hexene-2 which appears through rearrangement of two hydrogen atoms from the methylene groups in positions 1,4, converts into the system with isolated double bonds – cyclohexadiene-1,4.

As the result of this work, the authors have demonstrated that interaction of metallic sodium with 1,4-dibromocyclohexene proceeds according to Scheme (I), as the result of which only cyclohexadiene-1,3 is formed.

Thus, the authors have demonstrated that with equal possibility of formation of a six-membered ring with isolated or conjugated bond systems, the latter forms preferentially to the former.

EXPERIMENTAL

Synthesis of cyclohexadiene-1,3. 40.3 g of 1,2-dibromocyclohexane was added to 50 g of freshly-distilled, boiling quinoline in a flask equipped with dephlegmator, and the hydrocarbon evolved was distilled at 85°. The hydrocarbon was washed with dilute sulfuric acid (1 : 1), then with water, and dried over potash. There resulted 9.4 g (56%) of product boiling in the range 79-81°.

It was shown spectroscopically that the product did not represent uniform cyclohexadiene-1,3, but was found to be a mixture of cyclohexadiene-1,3 and cyclohexene and benzene. Separation of this mixture by simple fractionation was a task which could not be accomplished by the authors; the authors were therefore obliged to carry out rupture of hydrogenbromide from the dibromide by means of alcoholic alkali, whereupon it became evident that the yield of hydrocarbon is considerably lower, but the product is more uniform. 100 g of dibromocyclohexane was added in portions to a boiling solution of potassium hydroxide (60 g of potassium hydroxide in 315 ml of alcohol); reaction was accompanied by spontaneous heat evolution. After completion of addition of the dibromide, heating was carried out for 4 hours. The solution was filtered off from the potassium bromide precipitate, the filtrate diluted with water, and extracted with ether. The ether extract was washed free of alcohol with water, the ether solution dried over potash, and the ether distilled off.

The product was fractionated under atmospheric pressure, and it passed over almost completely within the range 154-156°:

n_D^{13} 1.4590, d_7^{13} 0.9180, MR_D 37.5.

This product was ethoxycyclohexene, described by a number of investigators [3]. 27 g (52%) was obtained.

Freshly fused potassium bisulfate (5% of the weight of ethoxy derivative) was added to 27 g of ethoxycyclohexene in a flask equipped with dephlegmator, and the mixture heated. The distillate was collected up to 90°, washed with water and the hydrocarbon which separated as a layer was dried over potash.

During fractionation, 14 g (82%) of fraction resulted:

B.p. 79-80°, n_D^{13} 1.4760, d_4^{13} 0.8400.

Judging from the constants [4,5], this product was taken to be pure cyclohexadiene-1,3.

Bromination of Cyclohexadiene-1,3. The calculated amount of bromine in chloroform (1 : 1) was added, with ice cooling, to a chloroform solution of cyclohexadiene-1,3 (1 : 1). The reaction mixture was washed with a dilute solution of sodium sulfite, then with water, and dried over calcium chloride. The chloroform was distilled off in vacuo. After distilling off the chloroform, the remaining oil was cooled; crystals precipitated from the oil, with varied melting points, depending upon conditions under which the solvent was distilled off. If the solvent was distilled off with heat, then the precipitated crystals possessed a m.p. of 96-98°, melting after recrystallization at 99-100°. If the solvent was distilled off in vacuo without heat, then the resulting crystals had a m.p. of 58-62°, with m.p. 64-66° after recrystallization. The oil which did not crystallize, after prolonged standing precipitated crystals which also melted at 64-66°.

Zelinsky [4], Crossley [5], Harries [6], Farmer and Scott [7] attribute the structure 1,4-dibromocyclohexene-2 to the dibromide with m.p. 99-100°, 105° and 108°, and the structure 1,2-dibromocyclohexene-3 to the dibromide with m.p. 64-68°.

It was established by the authors that 1,2-dibromocyclohexene-3, with m.p. 64-66°, yields two atoms of bromine with zinc dust when heated in dioxane, and converts into the cyclohexadiene-1,3. Under such conditions, the 1,4-dibromocyclohexene-2, with m.p. 99-100°, does not react with zinc dust at all, but in boiling xylene gives up both bromine atoms to metallic sodium, and also converts into cyclohexadiene-1,3. These facts are additional proof of the structure for each dibromide which the above-indicated authors have attributed to same.

Analytical data for bromine according to Carius, determination of molecular weight for the 99-100° product corresponded to the dibromide.

Attempts at a final and convincing solution of the question of structure for the dibromide of m.p. 99-100° by oxidation and hydrogenation did not give positive results. Upon oxidation with permanganate, the dibromide gave succinic acid, and upon ozonization and treatment of the ozonolysis products, only resinified products were obtained.

Hydrogenation over Raney nickel catalyst did not go.

Interaction of Metallic Sodium with 1,4-Dibromocyclohexene-2. Reaction was carried out in a flask with long dephlegmator. Three times the theoretical amount of freshly cut metallic sodium in the form of small lumps was placed in the flask. The xylene was twice distilled from metallic sodium.

In the xylene, reaction began only at the temperature of boiling xylene. Heating was discontinued, but the reaction mixture continued to boil with considerable spontaneous heat evolution for 10-15 minutes.

A fraction was collected in the range 70-90° from the reaction mixture. After fractionation of this cut on a column, 2 g of hydrocarbon was collected, which boiled at 79-80°:

n_D^{20} 1.4758, d_4^{20} 0.8380, MR_D 26.9.

For proof of structure, the hydrocarbon was condensed with maleic anhydride (m.p. 53°). 0.9 g of the hydrocarbon, 1.1 g of maleic anhydride and 2.5 ml of benzene were sealed in a test tube. 1.8 g of condensation product resulted with m.p. 141°, which coincides with the literature data [8].

SUMMARY

1. It has been established that cyclohexadiene-1,3 is formed upon interaction of 1,4-dibromocyclohexene-2 with metallic sodium.

2. It has been demonstrated that 1,4-dibromocyclohexene-2 does not react with zinc dust.

3. It has been demonstrated that for equal liklihood of formation of conjugated or of isolated bonds in a six-membered ring, formation of conjugated bonds takes preference.

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SYNTHESIS OF CYCLOPENTANOL

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Synthesis of cyclopentanol is carried out by reduction of readily accessible cyclopentanone by various procedures. However, this reaction is very frequently accompanied by considerable condensation of the ketone, as the result of which yields of the alcohol are usually low.

Wislicenus [1] prepared cyclopentanol in low yield by reducing cyclopentanone with sodium in moist ether. Venus-Danilova [2] demonstrated that to increase the yields of cyclopentanol it is necessary to free very thoroughly the ether from traces of ethyl alcohol. She was able to increase yields of cyclopentanol to 48-50%. Yields of the alcohol are not very constant, however. The reaction of tertiary butyl magnesium chloride with cyclopentanone leads to formation of cyclopentanol in yields of 11-60% [2]. Upon hydrogenation of the ketone over nickel at 125°, a complex mixture of products is formed, containing a small amount of cyclopentanol [3]. Hydrogenation over platinum catalyst in ether solution leads to formation of cyclopentane, cyclopentanol and other products [4]. According to the literature directions, cyclopentanol can be obtained in high yield by hydrogenation of the ketone in the presence of platinum under pressure [5].

The authors have investigated various methods for reducing cyclopentanone. It has been established that cyclopentane is formed predominantly upon hydrogenation over nickel catalyst supported by kieselguhr, at 125°. Hydrogenation over copper-chromo-barium catalyst at 160-170° led to formation of cyclopentanol in yield of 15%. Ketone condensation products form for the most part. Upon reducing the ketone with sodium in moist ether, the yields of alcohol fluctuated considerably, averaging about 30%.

By reduction of cyclopentanone with aluminum isopropylate under normal conditions it is possible to obtain cyclopentanol [6] in yield of 25-30%, in which case, however, the alcohol yields are not constant but are subject to considerable fluctuations, which is related to ketone condensation which proceeds simultaneously under the reaction conditions. A detailed study of this process has indicated that the extent of ketone condensation, and hence yields of alcohol, depend considerably upon duration of ketone contact with the aluminum isopropylate. The shorter the contact time, the less the extent of ketone condensation, and hence the higher the yield of alcohol. By carrying out this reaction under the conditions described below, it is possible to increase the yields of cyclopentanol to 62-66% with satisfactory reproducibility. This makes it possible to recommend the directions below as the appropriate laboratory method for preparing cyclopentanol.

EXPERIMENTAL

Aluminum isopropylate was prepared in the flask from 27 g of aluminum and 300 ml of anhydrous isopropyl alcohol [7]. The flask was then connected to a small dephlegmator and heated on an oil bath to the start of alcohol distillation, after which a solution of 27.5 g of cyclopentanone in 500 ml of isopropyl alcohol was added to the alcoholate. Addition of the cyclopentanone solution was carried out over a period of 12 hours. Temperature of the oil bath was maintained at 115-117°. After termination of addition of the ketone, heating of the flask was continued until the last portions of distillate ceased to give a positive reaction with dinitrophenylhydrazine. The flask was cooled in ice water, after which aqueous isopropyl alcohol (250 ml of alcohol and 70 ml of water) was added. The mixture was left at room temperature for the night, and the precipitate then filtered off. The precipitate on the filter was dissolved in sulfuric acid (80 ml of sulfuric acid and 500 ml of water), the acid solution extracted with ether, and the ether extract dried over potash.

The filtrate containing isopropyl alcohol, and almost all of the cyclopentanol were fractionated. After two fractionations, two fractions were isolated with b.p. 139-142°. From the ether extract a small amount of analogous products was isolated. The yield of crude cyclopentanol was 17.5 g (62.0%).

For characteristics, the fraction boiling at 140-141° was isolated.

d_4^{20} 0.9436, n_D^{20} 1.4520, MR_D 24.59. $C_5H_{10}O$. Calculated 24.61.

Combination Dispersion Spectrum [8].

840 (3), 894 (10), 938 (1), 1000 (3 b), 1034 (5), 1072 (3), 1187 (band), 1294 (band), 1344 (1), 1398 (1),

1449 (10), 1480 (1), 2870 (10), 2921 (10), 2961 (15).

SUMMARY

A method for preparing cyclopentanol has been described.

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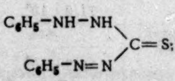
INVESTIGATION IN THE FIELD OF SUBSTITUTED THIOCARBAZONES

SYNTHESIS AND STUDY OF THE PROPERTIES OF ASYMMETRICAL THIOCARBAZONE DERIVATIVES

L. S. Pupko and P. S. Pelkis

Diphenylthiocarbazone (dithizone) (I) is widely used as an analytical reagent. With respect to this fact, the synthesis and investigation of the properties of its derivatives and analogs is of special interest.

Such investigations have led to the discovery of new organic reagents possessing certain properties differing from dithizone, and to a clarification of the effect of various substituents upon the analytical properties of such compounds [1-5].



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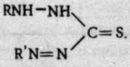


(II)

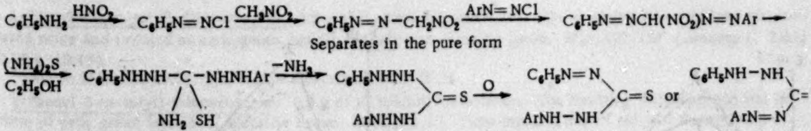
Unsymmetrical thiocarbazones of the type (II) have not been synthesized up to the present time due to the ab- of a method for their synthesis. In 1953, Irving and Bell attempted to prepare the unsymmetrical 1-phenyl-5-s-5-(2,4-dibromophenyl)-thiocarbazone by bromination of 1-phenyl-5-(2,4-dibromophenyl)-pharmazane and further action of the bromo derivative with sodium hydrosulfide. Due to insolubility of the resulting tribromoderivative, the authors failed to prepare the thiocarbazone [6].

The present authors have developed a method which permits preparation of a number of unsymmetrical thiocarbazones, among them 1-phenyl-(2,4-dibromophenyl)-thiocarbazone.

We were interested in the problems of how unsymmetrical thiocarbazones react with various cations, how disruption of the symmetry affects the character of the thiocarbazone absorption curves and their complexes with cations, and to what extent unsymmetrical thiocarbazones are stable to oxidation. The present work is devoted to a study of these problems.

The authors were not able to obtain unsymmetrical thiocarbazones according to the Fischer method [7] nor by the formazyl method [8], nor by interaction of arylhydrazines with thiophosgene. Only by the Bamberger method [8] for synthesis of symmetrical thiocarbazones, as modified by the authors, separating the nitroformaldehydrazone [9] in pure form, were the authors able to prepare the pure unsymmetrical thiocarbazones from the conjugation product between the diazonium salt and an alkaline solution of nitromethane.

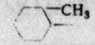
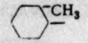
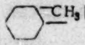
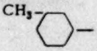
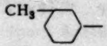
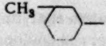
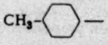
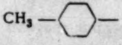
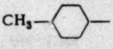
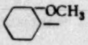
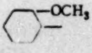
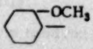
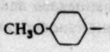
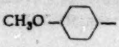
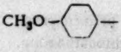
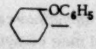
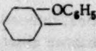
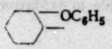
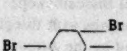
Unsymmetrical thiocarbazones, not described in the literature up to the present time, were prepared according to the following scheme:



The question of double bond location presented another problem of interest.

In the table there are presented absorption maxima and molar extinction coefficients for the unsymmetrical thiocarbazones (II) synthesized by the present authors, and their corresponding symmetrical thiocarbazones. The symmetrical thiocarbazones were synthesized by methods described in the literature, and investigated spectrophotometrically by the authors for the first time. Thiocarbazones are soluble in benzene, chloroform and carbon tetrachloride with a green coloration.

Absorption curves for the thiocarbazones (Figs. 1,2 and 3) were determined on a Bellirham and Stanley spectrophotometer. For the measurements, solutions of the dyes in benzene were taken of concentration 6.6 X 10^{-5} moles per liter.

No.	R	R'	ε max	λ_1	λ_2
1	C_6H_5	C_6H_5 [10]	$7.9 \cdot 10^4$	450	620
2	C_6H_5		$7.5 \cdot 10^4$	460	626
3		 [2]	$12.1 \cdot 10^4$	472	633
4			$12.8 \cdot 10^4$	464	635
5	C_6H_5	 [2]	$9.6 \cdot 10^4$	455	625
			$14.4 \cdot 10^4$	465	631
7	C_6H_5		$11.2 \cdot 10^4$	458	626
8		 [5]	$16.8 \cdot 10^4$	486	659
9	C_6H_5		$13.8 \cdot 10^4$	470	640
10		 [5]	$17.3 \cdot 10^4$	476	646
11	C_6H_5		$11.1 \cdot 10^4$	470	632
12		 [5]	$16.8 \cdot 10^4$	490	650
13	C_6H_5		$11.7 \cdot 10^4$	460	635
14	C_6H_5		$3.8 \cdot 10^4$	435	630

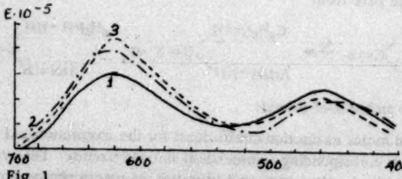


Fig. 1.

1) 1-phenyl-5-(o-tolyl)-thiocarbazone;
2) 1-phenyl-5-(m-tolyl)-thiocarbazone;
3) 1-phenyl-5-(p-tolyl)-thiocarbazone.

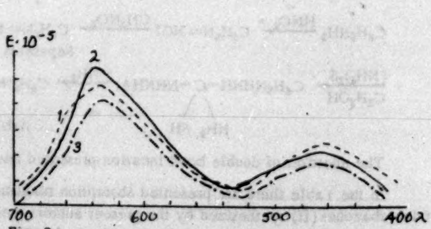


Fig. 2.

1) 1-phenyl-5-(phenoxyphenyl)-thiocarbazone;
2) 1-phenyl-5-(o-methoxyphenyl)-thiocarbazone;
3) 1-phenyl-5-(m-methoxyphenyl)-thiocarbazone.

As can be seen from the Table, the absorption maxima for all unsymmetrical thiocarbazones are shifted to the long wave-length range, as compared with the absorption maxima for dithizone. If one compares the positions of the long wave absorption maxima for the unsymmetrical thiocarbazones with the absorption maxima for the corresponding symmetrical derivatives, it will be found that the maxima for unsymmetrical lie for the most part in the middle between the maxima for the symmetrical.

All unsymmetrical thiocarbazones give intracomplex compounds with Pb, Hg, Zn and Ag cations, soluble in organic solvents.

On the absorption curves for these intracomplex compounds, measured in benzene, are two maxima in the short wave range, shifted in the direction of the long waves as compared with the maxima for the intra-complex of dithizone with the same cation.

EXPERIMENTAL

Synthesis of Nitroformaldehydrazone. Prepared according to Bamberger [9]. Fine crystals, orange in color, with m.p. 87-91°. Yield was 4.9 g (29.6 %).

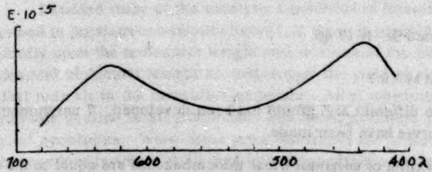


Fig. 3. 1-Phenyl-5-(2,4-dibromophenyl)-thiocarbazone.

1-Phenyl-5-(o-phenoxyphenyl)-thiocarbazone. 1.34 g of o-phenoxyaniline [5] was diazotized by dissolving in 0.79 g of concentrated hydrochloric acid and 4 ml of water with addition of 0.6 g of sodium nitrite in 2 ml of water, at 0°. 0.42 g of nitroformaldehydrazone dissolved in 35 ml of ethyl alcohol was added to the resulting diazo solution, and 30 ml of water then added to the reaction mixture. The formazyl derivative, dark-red in color, precipitated. The precipitate was filtered, washed with water, alcohol, and ether. Yield was 0.8 g (31.7%).

The formazyl derivative was suspended in a small amount of methyl alcohol, and gaseous ammonia and hydrogen sulfide passed through the alcoholic solution until the red color of the solution had turned to yellow. The solution was poured into ice water and the precipitated light-yellow solid filtered, washed with water, and dried at room temperature. The precipitate was treated with 2.5% alcoholic solution of potassium hydroxide and the solution filtered. The thiocarbazone was precipitated from solution with 1% H_2SO_4 from an alcoholic solution of potassium hydroxide.

Fine, green-black crystals with metallic lustre. M.p. 133-134° (decomp.). Yield was 0.3 g (12%).

Found %: N 15.90, 15.73. $C_{19}H_{16}ON_4S$. Calculated %: N 16.09.

1-Phenyl-5-(o-tolyl)-thiocarbazone and 1-phenyl-5-(m-tolyl)-thiocarbazone were synthesized under conditions similar to that for the 1-phenyl-5-(o-phenoxyphenyl)-thiocarbazone.

1-Phenyl-5-(o-tolyl)-thiocarbazone. 0.8 g of o-toluidine was taken. The red formazyl derivative resulted. After 3 precipitations, the thiocarbazone was in the form of dark-red needles with metallic lustre. M.p. was 129-130° (decomp.). Yield was 0.25 g (12.4%).

Found %: N 20.84, 20.58. $C_{14}H_{14}N_4S$. Calculated %: N 20.74.

1-Phenyl-5-(m-tolyl)-thiocarbazone. 0.8 g of m-toluidine was taken. The resulting thiocarbazone was precipitated twice and isolated as dark-green, needle crystals with metallic lustre. M.p. 127-128° (decomp.). Yield was 0.27 g (13.4%).

Found %: N 20.43, 20.56. $C_{14}H_{14}N_4S$. Calculated %: N 20.74.

1-Phenyl-5-(p-tolyl)-thiocarbazone. 0.8 g of p- toluidine was taken. The resulting thiocarbazone was in the form of dark green crystals of metallic luster. M.p. 132 13[illegible]° (decomp.). Yield of purified thiocarbazone was 0.[illegible] g (1[illegible].9%).

Found %: N 20.35, 20.31. $C_{14}H_{14}N_4S$. Calculated %: N 20.74.

1-Phenyl-5-(o-anisyl)-thiocarbazone. 1.17 g of o-anisidine was taken. The resulting thiocarbazone was purified by four-fold precipitation and isolation in the form of brown needles with metallic luster. M.p. was 137-138° (decomp.). Yield was 0.25 g (9.2%).

Found %: N 19.20, 19.35. $C_{14}H_{14}ON_4S$. Calculated %: N 19.59.

1-Phenyl-5-(p-anisyl)-thiocarbazone. 1.17 g p-anisidine. After 3 precipitations, thiocarbazone, dark-green crystals with metallic luster, m.p. 139-140 (decomp.). Yield 0.3 g (11%).

Found %: N 19.51, 19.40. $C_{14}H_{14}ON_4S$. Calculated %: N 19.59.

1-Phenyl-5-(2,4-dibromophenyl)-thiocarbazone. 1.25 g of 2,4-dibromoaniline dissolved in 2.5 g of fuming nitric acid and 4 ml of water was diazotized with 0.37 g of sodium nitrite in 2 ml of water at 0-2°. The resulting diazo solution was added to a mixture of 25 g of crystalline sodium acetate and 12.5 ml of glacial acetic acid, with continuous stirring. 0.15 g of the hydrazone diluted in 5 ml of methyl alcohol was then added to the mixture. The solution became red instantaneously, and the formazyl derivative precipitated — dark-red crystals. Stirring was continued for 1 hours. The precipitate was filtered, washed with water, methyl alcohol and ether.

Reduction of the nitroformazyl and oxidation of the resulting thiocarbazide to the 1-phenyl-5-(2,4-dibromophenyl)-thiocarbazone was carried out according to the procedure given for 1-phenyl-5-(o-phenoxyphenyl)-thiocarbazone. The thiocarbazone was in the form of red crystals with metallic lustre. M.p. 99° (decomp.). Yield was 0.26 g (11%).

Found %: N 13.29, 13.34. $C_{13}H_{10}N_4Br_2S$. Calculated %: N 13.49.

SUMMARY

A method for synthesizing thiocarbazones with two different aryl groups has been developed. 7 unsymmetrical thiocarbazones have been prepared. Their absorption curves have been made.

It has been found that values for the absorption maxima of unsymmetrical thiocarbazones are equal to the arithmetic mean of the maxima for the two corresponding paris of symmetrical thiocarbazones.

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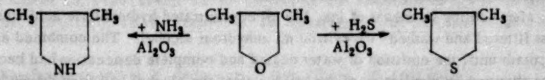
CONVERSION OF 3,4-DIMETHYLFURANIDINE INTO 3,4-DIMETHYLTHIOPHANE AND 3,4-DIMETHYLPYRROLIDINE. XLII.

Yu. K. Yuryev and G. Ya. Kontradyeva

Detailed study of the catalytic conversion of furanidine homologs into thiophane and pyrrolidine homologs, described in previous communications [1,2] made it possible to establish that the duration of these reactions depends chiefly upon the molecular weight and structure of the initial oxide. Where mono- and dialkylfuranidine isomers of identical molecular weight are concerned, the yield of ultimate conversion products depends upon the location of the alkyl radicals in the furanidine molecule. Alkyl substitutes in the α-carbon atom of the furanidine ring cause a considerable decline in alkylthiophane and alkylpyrrolidine yields relative to that of thiophane proper and, correspondingly, of pyrrolidine. When these same substitutes are in the β-position, they affect, but to a much more limited degree, the reactions in which sulfur and nitrogen-containing heterocyclic compounds are formed from their oxygen-containing analogs. Thus, for example, 3-methyl-furanidine converts to 3-methylthiophane with a 81% yield, while 2-methyl furanidine gives a 69% yield of 2-methylthiophane; 3,3-dimethylfuranidine gives a 73% yield of 3,3-dimethylthiophane, and its isomers, 2,4- and 2,2-dimethylfuranidine give 2,4- and 2,2-dimethylthiophanes in yields of 58% and 27% respectively.

The present work will show that 3,4-dimethylfuranidine, in which both methyl groups are in the beta position, as they are in 3,3-dimethylfuranidine, readily converts, in the conditions of catalytic conversion of oxygen-containing heterocyclics into rings with other hetero-atoms, into the corresponding compounds of the thiophane and pyrrolidine series – 3,4-dimethylthiophane (71% yield) and, correspondingly, 3,4-dimethylpyrrolidine (42% yield), hitherto not described in the literature.



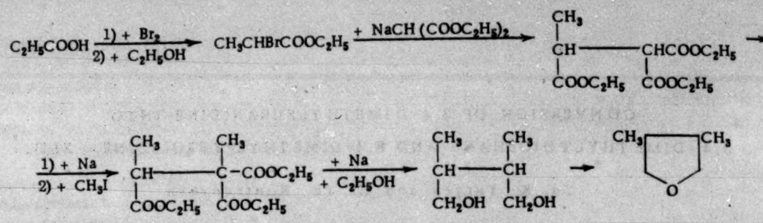
We obtained 3,4-dimethylfuranidine, also not described in the literature, by dehydration of 2,3-dimethylbutanediol-1,4, which, in its turn, had been obtained by reduction of sodium in triethyl ester butane-2,2,3-tricarboxylic acid alcohol. Longinov [3], it is known, described the reduction of Na in tricarboxylic ether alcohols of the $(COOR_1)_2C(R)-$ $-CH_2COOR_1$, type, resulting in the production of substituted tetramethyleneglycol having, as a general formula $CH_2OH-CH(R)-CH_2-CH_2OH$.

The mechanism of this reaction was studied, somewhat later, by Dzirkal, a pupil of Longinov. Studying the analogous cleavage of substituted malonic esters, Dzirkal showed that, when reacted with hydrogen, one carboethoxyl group splits off at the moment that $RHC(COOR_1)_2$ separates from the ester, and a monocarboxylic acid ester is formed, which is then reduced in the usual way [4]. The dicarboxylic acid esters and then the corresponding glycols are obtained analogously from the tricarbonic acid esters. There is no reference in the literature to reduction of the tricarboxylic esters of the general formula $(COOR_1)_2(R)C-CH(R)-COOR_1$, although our reduction of the triethyl ester of butane-2,2,3-tricarboxylic acid demonstrated that it follows the same course described by Longinov and Dzirkal for the conversion of monoalkyltricarboxylic tri- or monoalkyldicarboxylic esters with two carbalkoxyl groups at the same carbon atom, and results in the corresponding butanediol-1,4, substituted in positions 2 and 3.

EXPERIMENTAL

Synthesis of 3,4-dimethylfuranidine

The complete course of synthesis of 3,4-dimethylfuranidine performed in the present study included the following stages:



The ethyl ester of α-bromopropionic acid was obtained by the Zelinsky method [5]; b.p. 154-157° (756 mm).

Butane-2,3,3-tricarboxylic acid ethyl ester (butanetricarboxylic ester). 120 g (0.75 g/mole) malonic ester, and then, by drops and with stirring, 136 g (0.75 mole) α-bromopropionic acid ester were added to an alcohol solution of sodium ethylate, composed of 18 g (0.75 g-at.) sodium in 270 ml anhydrous ethyl alcohol. The reaction mixture was heated over a bath of boiling water until a test of the solution no longer showed a neutral reaction to phenolphthalein, and was then cooled to room temperature. Another 18 g sodium was added to the cold mixture in small pieces, and, after complete solution had been obtained, 114 g (0.8 mole) methyl iodide was added from a dropping funnel. The mixture was heated, with constant stirring, for 2 hours, and then permitted to stand overnight. The alcohol was then distilled off in a vacuum (over a water bath), and water was added to the residue to dissolve the sodium bromide. After the butane-2,3,3-tricarboxylic acid ethyl ester had been removed from aqueous solution and desiccated with calcium chloride, it was distilled in a vacuum b.p. 137-139° (4 mm). Yield 140 g (66%).

Data from the literature [6]: b.p. 205-215° (125 mm).

2,3-Dimethylbutanediol-1,4. 40 g (1.74 g-at) Na, in two large chunks, was placed in a round-bottomed flask with horned adapter and copper reflux condenser; to this was added, quickly a solution of 28 g (0.102 mole) butanetricarboxylic ester in 400 ml anhydrous alcohol. At the conclusion of the vigorous reaction, an oil bath heated to 150° was placed beneath the flask, and the mixture was heated at this temperature for another 30 minutes after complete dissolution of the sodium; 20 ml water was then added and the reaction mixture boiled for another 20 minutes, upon which, after cooling by means of ice, 190 ml concentrated hydrochloric acid was added. The residue of sodium chloride was filtered and washed 3 times in 60 ml anhydrous alcohol. The combined alcohol solutions were boiled with calcined potash until the emission of water ceased and complete desiccation had been obtained. 2,3-Dimethylbutanediol-1,4 was obtained by distillation of the residue after the alcohol had been driven off in a vacuum (over a water bath):

B.p. 128-130° (12 mm), n_D^{20} 1.4563, d_4^{20} 0.9856, MR$_D$ 32.62. $C_6H_{14}O_2$. Calculated: 32.96.
Found %: C 59.24, 59.17; H 11.80, 11.70. $C_6H_{14}O_2$. Calculated %: C 60.98; H 11.88.

Yield 4.6 g (38%).
2,3-Dimethylbutanediol-1,4 is not described in the literature.

3,4-Dimethylfuranidine. 6 g 2,3-dimethylbutanediol-1,4 and 0.6 g aluminosilicate cracking catalyst were heated at 200° in a distillation flask with a tightly-sealed branch pipe. The distillate was desiccated with calcium chloride and distilled over sodium from a flask with a dephlegmator. The 3,4-dimethylfuranidine (4 g, 78%) had the following constants:

B.p. 108.4-108.8° (760 mm), n_D^{20} 1.4183, d_4^{20} 0.8583, MR$_D$ 29.43. $C_6H_{12}O$. Calculated: 29.35.
Found %: C 71.75, 71.77; H 12.05, 12.15. $C_6H_{12}O$. Calculated %: C 71.99; H 12.09.

3,4-Dimethylfuranidine is not described in the literature.

3,4-Dimethylthiophane

7.7 g 3,4-dimethylfuranidine was passed over aluminum oxide in a stream of hydrogen sulfide at 350°, at a rate of 0.5 ml/min. The catalyst was saturated with alkali and extracted by ether. The ether extract was desiccated with fused caustic potash. Distillation of the reaction product gave 6.4 g (71%) 3,4-dimethylthiophane:

B.p. 155.4-156° (756 mm), n_D^{20} 1.4908, d_4^{20} 0.9446, MR$_D$ 35.55. $C_6H_{12}S$. Calculated: 35.68.
Found %: C 62.19, 62.15; H 10.68, 10.68; S 27.58, 27.56. $C_6H_{12}S$. Calculated %: C 62.00; H 10.41; S 27.59.

The derivative with $HgCl_2$ had a boiling point of 152 (from anhydrous alcohol).

3,4-Dimethylthiophane is not described in the literature.

3,4-Dimethylpyrrolidine

6 g 3,4-dimethylfuranidine was passed over activized aluminum oxide in a stream of ammonia at 315° and at a rate of 0.25 ml/min. The flask was cooled to −40°, and at the end of the reaction it was connected to a reflux condenser and the ammonia gradually evaporated at room temperature. The residue was saturated with caustic potash and extracted by ether. After the ether had been driven off, 2.5 g (42%) 3,4-dimethylpyrrolidine was isolated by redistillation of the residue after caustic potash desiccation of the ether extract.

B.p. 121-122° (750 mm), n_D^{20} 1.4400, d_4^{20} 0.8439, MR_D 30.98. $C_6H_{13}N$. Calculated: 31.31.

Picrate: m.p. 123-124° (from alcohol).
Found %: N 17.02, 17.42. $C_{12}H_{16}O_7N_4$. Calculated %: N 17.03.

3,4-Dimethylpyrrolidine is not described in the literature.

SUMMARY

1. 3,4-Dimethylfuranidine, the synthesis of which is described for the first time in this study, converts smoothly to 3,4-dimethylthiophane (71% yield) and 3,4-dimethylpyrrolidine (42% yield) in conditions of catalytic conversion of oxygen-containing heterocyclics into rings with other hetero-atoms.

2. The conversions of 3,4-dimethylfuranidine described proceeded in a manner analogous to the conversion of 3,3-dimethylfuranidine; the similarity of conduct of these γ-oxide isomers confirms the concept that alkyl substitutes at the β-carbon atom of the furanidine ring, affect but weakly the course of catalytic conversion into nitrogen and sulfur-containing heterocyclic compounds.

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SYNTHESIS OF γ-FORMYLPYRIDINE AND ISONICITINIC ACID

M. V. Rubtsov, E. S. Nikitskaya and A. D. Yanina

Oxidation of the appropriate methyl derivatives of selenium dioxide readily produces quinoline aldehydes [1]. This reaction is most frequently performed in xylol or without a solvent.

With regard to the pyridine aldehydes, there is an indication in the literature that they cannot be successfully obtained by an analogous process from the appropriate methyl derivatives, as the oxidation process does not end at the aldehyde stage, but proceeds to the production of pyridine carboxylic acids.

We questioned this conclusion. We decided to attempt to select conditions under which oxidation of the methyl derivatives by selenium dioxide would result in production of the corresponding aldehydes. γ-Formylpyridine was the first to engage our interest, as this compound is of considerable importance to the synthesis of an entire series of pyridine γ-derivatives, and our interest was heightened by the fact that no convenient method of obtaining it had been described in the literature [4].

The substance with which we began was the β-picoline fraction, freed of its α,α-lutidine, and constituting a mixture of β-picoline (about 60 %) and γ-picoline (about 40%).

Our experiments showed that treatment of this mixture with selenium dioxide results in selective oxidation of γ-picoline with the formation of γ-formylpyridine and isonicotinic acid.

When 1 mole of selenium dioxide was reacted with 1 mole of γ-picoline in dry toluol, about 13% γ-formylpyridine and about 33% isonicotinic acid was produced. When a doubled quantity of selenium dioxide was used in the reaction, only isonicotinic acid was formed, with a yield of up to 75%. Approximately the same results were obtained with oxidation in xylol. The isonicotinic acid was precipitated with the selenium, and the γ-formylpyridine remained in solution in the toluol, from which it was readily isolated in the form of its bisulfite derivative. Oxidation in organic solvents – toluol or xylol – proceeds rapidly and requires only an hour or two. Oxidation proceeds even more rapidly without a solvent, but it results in severe resinification of the reaction mass. It is of interest to note that oxidation in an aqueous medium resulted in the production only of isonicotinic acid, regardless of the quantity of selenium dioxide employed. Under appropriate conditions, the acid yield attained 80%.

Oxidation in water goes slower than in an organic solvent, is concluded in six hours, and gives good quality isonicotinic acid not requiring further purification. Moreover, oxidation may be conducted in water even in the presence of α,α-lutidine, as this compound does not oxidize under these conditions.

The aqueous oxidation method permits the use as oxidizing agent of 50% selenic acid, obtained by processing sulfuric acid production wastes.

EXPERIMENTAL

I. Production of γ-formylpyridine

Oxidation of γ-picoline. 20 g selenium dioxide was gradually added, with vigorous stirring, to a mixture of 52.5 g β-picoline fraction from which the α,α-lutidine had been removed and 65 ml dry toluol, heated to boiling (120°). The reaction mass was heated and boiled for two hours (constant stirring). During this process, the temperature gradually dropped to 97°. At the conclusion of the reaction, the mass was cooled and the deposit of selenium and isonicotinic acid was filtered, washed twice in 20 ml toluol, and the toluol wash mixed with the main filtrate.

Isolation of γ-formylpyridine. The toluol filtrate, containing the γ-formylpyridine, was transferred to a glass to which 15 ml of a 50% sodium bisulfite solution was added, the whole cooled to 0°, stirred until formation of a viscous mass at the bottom of the glass, the liquid poured off and 50 ml alcohol added to the residue. It was then carefully mixed, filtered, washed in 15 ml alcohol and dried in air. The product was 7.6 g impure sodium salt of γ-pyridylhydroxymethanesulfonic acid, from which 3.02 g γ-formylpyridine was obtained by the method described above [5]. The yield was 12.7% based on γ-picoline.

Isolation of isonicotinic acid. The precipitate, containing metallic selenium and isonicotinic acid, was gradually poured into 75 ml of a 15% sodium carbonate solution, constant stirring. When this was done, the selenium was filtered out of the solution, washed in 30 ml water, and the wash water was mixed with the filtrate. The filtrate, consisting of an isonicotinic acid sodium salt solution, was treated with activated carbon and filtered, the clear, colorless solution yielding isonicotinic acid when acetic acid was added. 9.27 g isonicotinic acid was obtained, or a 33% yield, if measured in terms of γ-picoline.

12.9 g metallic selenium was obtained (91%).

II. Production of isonicotinic acid.

Oxidation in an organic solvent. 193.5 g selenium dioxide was added, bit by bit, but steadily, in the course of 30 to 45 minutes, to a vigorously-stirred mixture of 180 g β-picoline fraction freed of α,α-lutidine, with 120 ml dry xylol, heated to boiling (140°). The reaction mass was heated for an hour at boiling point, during which its temperature fell to 105-108°. The mass was then cooled, and the precipitate filtered and washed in 200 ml water and 50 ml alcohol. The gray precipitate obtained, consisting of a mixture of selenium and isonicotinic acid, was processed as above. The product was 71.4 g isonicotinic acid (75 %) with m.p. 306-308° (in a sealed capillary tube) and 126 g metallic selenium (91.5%).

Oxidation in an aqueous medium. 387 g of a 50% aqueous solution of selenium dioxide was added from a dropping funnel, with stirring, to 180 g β-picoline fraction freed of its α,α-lutidine and heated to boiling (138-140°). This was done at a rate that enabled the reaction mass to boil evenly. The temperature of boiling gradually dropped to 104-105°. After all the selenium dioxide solution was added, the reaction mass was boiled for another six hours, after which the water and β-picoline was driven off. This was done while stirring. 180 ml water was added to the dry residue, mixed until a homogeneous mass was formed, and filtered. Further processing was the same as that described above. The yield of isonicotinic acid was 76 g, or 80%, measured in terms of γ-picoline. The selenium yield was 126 g (91.5%).

SUMMARY

1. Conditions were discovered for the production of γ-formylpyridine by selective oxidation of γ-picoline by selenium dioxide in the presence of β-picoline.

2. Two methods of producing isonicotinic acid were developed which make it possible to obtain a 75-80% yield of this compound, measured in terms of γ-picoline.

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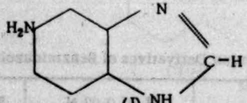
SYNTHESIS AND PROPERTIES OF CERTAIN BENZIMIDAZOLE DERIVATIVES

I. REACTION OF 1,2,4-TRIAMINOBENZENE WITH CARBOXYLIC ACIDS

B. A. Porai-Koshits and G. M. Kharkharova

This communication is devoted to the study of the reaction of 1,2,4-triaminobenzene with carboxylic acids, and also to investigation of the properties of 5-aminoderivatives of benzimidazole. Synthesis of the latter was undertaken at the suggestion of N. V. Lazarev with the purpose of studying their pharmacological action.

It is known that [2] lengthy boiling of the free base 1,2,4-triaminobenzene with formic or acetic acid will produce, respectively, 5-amino-and 2-methyl-5-aminobenzimidazole (I and II)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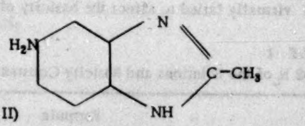

(II)

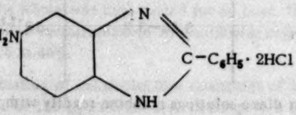
As we have demonstrated, these compounds are also readily prepared by boiling 1,2,4-triaminobenzene [1] dichloride with the acids mentioned above.

We found no references to the condensation of 1,2,4-triaminobenzene with aromatic (i.e., benzoic) and aliphatic-aromatic (phenylacetic and hydrocinammic) acids. However, reaction of these acids with the ortho-diamines of the benzene series proceeds rather smoothly in tubes under pressure, in the presence of hydrochloric acid [3,4].

The concentration of the latter to be used depends upon the basicity of the ortho-diamine: the greater the basicity, the lower the concentration of hydrochloric acid required to attain the maximum benzimidazole derivative yield [3,4].

The basicity of 1,2,4-triaminobenzene ($k=10^{-7.9}$), is considerably higher than that of 3,4-toluylene diamine ($k=10^{-9.0}$), o-phenylene diamine ($k=10^{-9.15}$) and 3,4-diaminochlorobenzene ($k=10^{-9.7}$) [5].

However, to obtain the maximum reaction product yield from carboxylic acids and 1,2,4-triaminobenzene a higher concentration of hydrochloric acid is needed than for the attainment of the highest yield of condensation products of these acids with the given ortho-diamines. At low concentrations (5-15 %) of hydrochloric acid, 1,2,4-triaminobenzene reacts with benzoic and hydrocinnamic acids to give a negligible yield of 2-phenyl-5-amino- (III) and 2-(β-phenylethyl)-5-amino-benzimidazole (IV) chlorohydrates: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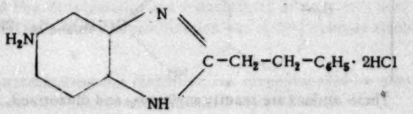
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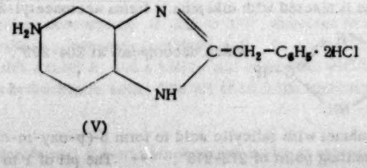
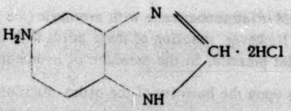
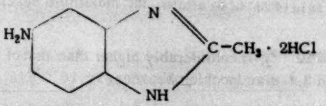
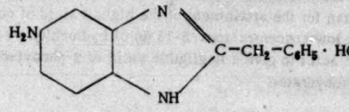
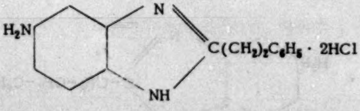

(V)

Concentration of this compound with phenylacetic acid gives much better results under these conditions. Thus, 2-benzyl-5-amino-benzimidazole chlorohydrate (V) was obtained in a yield of 25% of the theoretical in the presence of 15% hydrochloric acid. Detailed study of this reaction revealed that the yield of (V) depended to a considerable degree not only on the hydrochloric acid concentration, but on the temperature and the duration of the heating of the reaction mass. The optimum yield (74-80%) of 2-benzyl-5-amino-benzimidazole (V) in the presence of 30-35% hydrochloric acid was obtained by heating the initial products in tubes at 150-160° under pressure for seven hours. Lower duration and temperature of heating of the reaction mass led to a drop in yield, while an increase in these factors led to a reduction in the quality of the final product. These were the conditions in which 1,2,4-triaminobenzene was reacted with hydrocinammic (60-70%) and benzoic (10-15%) acids.

2-Benzyl-5-amino-(V) and 2-(β-phenylethyl)-5-amino-benzimidazole (IV) chlorides were first obtained by us. Their structure was determined by the process of synthesis and was confirmed by potentiometric titration by a 0.1 N solution of caustic soda, and also by combustion with nitrogen. Considerable difficulties were encountered in freeing the 5-amino derivatives of benzimidazole from impurities. All the sulfides (I, II, III, IV, V) were readily soluble in water, slightly soluble in alcohol and virtually insoluble in ether and benzene. Their constants of basicity were low, as were their pH in aqueous solution (Table 1). The most basic of the amines adduced in Table 1 was, as might have been expected, 2-methyl-(II) and 2-(β-phenylethyl)-5-amino-benzimidazole (IV). In the latter instance the phenyl radical virtually failed to affect the basicity of the benzimidazole derivative.

TABLE 1

pH 0.02 N of the Solutions and Basicity Constants of Certain 5-Amino Derivatives of Benzmidazole (I, II, III and IV)

No.	Formula	pH of 0.02 N solution	Basicity K at 25°
1		1.5–2.0	$10^{-7.4}$
2		2.5–2.8	$10^{-7.2}$
3		3.0–3.1***	$10^{-7.4}$
4		3.15–3.2	$10^{-7.2}$

These amines are readily acylated* and diazotized. Their diazo solutions combine readily with various azo components.** Thus, for example, they form a crimson dye with Azotol A.

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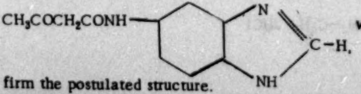
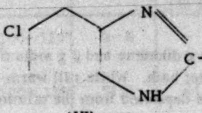
* When 5-amino-benzimidazole is reacted with diketene it forms acetoacetyl-5-amino-benzimidazole



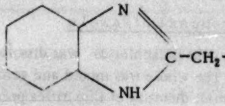
which decomposes at 204-205°. Results of analysis for nitrogen confirm the postulated structure.

** 5-Diazo-benzimidazole combines with salicylic acid to form 5-(p-oxy-m-carboxy-benzeneazo)-benzimidazole a yellow azo compound with a melting point of 272-273°. *** The pH of 1 to 3% solutions falls from 3 to 2.7.

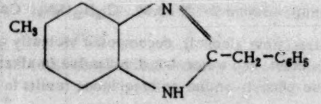
We obtained interesting findings when we compared the constants of basicity of the above-mentioned o-phenylenediamine derivatives to their reactive capacities in concentrated hydrochloric acid. We observed that the yields of the condensation products of phenylacetic acid and 3,4-diaminochlorobenzene, o-phenylenediamine and 3,4-toluylenediamine (VI, VII, VIII) declined inversely to the rise in basicity constant of orthodiamines (Table 5). 1,2,4-Triaminobenzene behaves differently under these conditions, however. It condenses with phenylacetic acid much more readily than does 3,4-toluylenediamine, although its basicity is considerably higher than that of the latter (Table 5).



(VI)



(VII)



(VIII)

EXPERIMENTAL

1,2,4-Triaminobenzene dichloride

1,2,4-Triaminobenzene was produced analogously to the production of o-phenylenediamine [6,7] by the reduction of 4-nitro-1,3-phenylenediamine by sodium sulfide.

3 parts 4-nitro-1,3-phenylenediamine was added to an aqueous solution, filtered for impurities, consisting of 7 parts 60% melted sodium sulfide and 13 parts water. With the mixer in constant motion, the mixture was heated to 108-109°, upon which heating was interrupted for a period, as the temperature of the flask contents rose spontaneously to 110-112°. That temperature was then maintained for four hours by heating until reduction of the 4-nitro-1,3-phenylenediamine was completed. Cooling of the reaction mass proceeded at room tempearture. The 1,2,4-triaminobenzene crystals were filtered, washed in a small amount of ice water, and with an alcohol-ether mix (1 : 1)* and dissolved in hot ethyl alcohol. The alcohol solution was filtered free of contaminants, and the 1,2,4-triaminobenzene dichloride was precipitated by twice its volume of 35% hydrochloric acid.

1,2,4-Triaminobenzene dichloride was obtained in the form of yellow-gray needles, decomposing at 243-246° with a yield of about 80%.

0.1960 g sub.: 20.01 ml 0.1 N NaOH. $C_6H_3(NH_2)_3 \cdot 2HCl$. Calculated: 0.1 N NaOH 20.0 ml.

5-Amino-benzimidazole Dichloride

a) 19.6 g 1,2,4-triaminobenzene dichloride and 12 ml 90% cinnamic acid were heated for 8 hours over a water bath. 100 ml 15% hydrochloric acid was added after cessation of generation of gaseous hydrogen chloride (Congo paper test); the whole was then boiled for an hour, filtered free of impurities and concentrated in a vacuum until the onset of 5-amino-benzimidazole hydrochloride crystallization. After recrystallization out of 50% aqueous alcohol the yield was 35 to 40%.

b) Heating of equimolecular quantities of 1,2,4-triaminobenzene dichloride and cinnamic acid in tubes under pressure and at 160 to 170° for five hours gave a 60% yield of 5-amino-benzimidazole hydrochloride.

0.2000 g sub.: 9.08 ml 0.935 N solution $NaNO_2$. Found amine, %: 100.13.
0.1890 g sub.: 18.1 ml 0.1 N NaOH. $C_7H_7N_3 \cdot 2HCl$. Calculated:18.2 ml 0.1 N NaOH.

The needles were gray in color, decomposed at 315 to 317°, dissolved freely in water and slightly in alcohol. They diazotized readily, and the diazo compounds combined well in an acetic acid medium, with various azo components (forming a crimson dye with Azotol A, and a yellow azo compound with salicyclic acid). These compounds decomposed upon long heating in hydrochloric acid. The pH of an 0.5% aqueous solution was 1.5-2.0.

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* After crystallization out of chloroform 1,2,4-triaminobenzene melts at approximately 100° (decomposing).

5-(p-Oxy-m-carboxy-benzene-azo)-benzimidazole

3.75 g of 5-aminobenzimidazole dichloride was diazotized in the usual way [8]. The diazo solution was filtered and added to a solution of 2.88 g sodium salicylicate and 8 g soda in 35 ml water. They combined slowly. An azo compound, yellow in color, was filtered off after 3 days. The yield was 3.72 g.

The small yellow needles, with a melting point of 272-273° (from alcohol), are slightly soluble in water and 10% hydrochloric acid.

0.1076 g sub.: 18 ml N_2 (21°, 775 mm). Found %: N 19.4. $C_{14}H_{10}O_3N_4$. Calculated %: N 19.8.

Acetoacetyl-5-amino-benzimidazole

2 g 5-amino-benzimidazole hydrochloride was dissolved in 15 ml water, 4 g diketene and 8 g sodium acetate being added to this solution. The whole was mixed and gently heated over a water bath. While still warm, the solution was filtered free of the small quantity of impurities present. The precipitate deposited from the solution when it cooled was filtered, washed with water and then alcohol, desiccated and recrystallized. The yield was 1.2 g (47%).

0.0790 g sub.: 12.8 ml N_2(20°, 764 mm). Found %: N 18.80. $C_{11}H_{11}O_2N_3$. Calculated %: N 19.80.

The needles, small, slender and colorless (from alcohol), decomposed violently at 204-205°; they were slightly soluble in cold and hot chloroform, benzene, ether, and water, but did dissolve in alkalis and acids. Combination with diazotized 1-methyl-amino-4-(p-amino-phenyl)-amino-anthraquinone results in a green dye.

2-Methyl-5-amino-benzimidazole dichloride

It was produced: (a) by long heating of equimolecular quantities of acetic acid and 1,2,4-triaminobenzene hydrochloride in the presence of 14% hydrochloric acid. The reaction mass was filtered for contaminants and condensed over a water bath, giving a yield of about 30%; (b) by heating equimolecular quantities of 1,2,4-triaminobenzene and glacial acetic acid in tubes under pressure for 2 hours at 170-175°. The reaction mass was digested with 5% hydrochloric acid. The aqueous solution was filtered free of contaminants and condensed in vacuum in a stream of carbon dioxide over a water bath.

0.1747 g sub.: 7.8 ml 0.0995 N $NaNO_2$. Amine content found %: 99.0. 0.2060 g sub.: 18.4 ml 0.1 N NaOH. $C_8H_9N_3 \cdot 2HCl$. Calculated: 18.6 ml 0.1 N NaOH.

These gray needles, decomposing at 314-315°, dissolved freely in water, slightly in alcohol. The picrate melted at 213-214° (from alcohol), as indicated in the literature [2].

Reaction of 1,2,4-triaminobenzene with phenylacetic acid

a) Effect of temperature of heating upon 2-benzyl-5-amino-benzimidazole yield. Equimolecular quantities of 1,2,4-triaminobenzene (1.96 g) dichloride and phenylacetic acid (1.36 g) were heated for 7 hours in a sealed tube under pressure with 10 ml concentrated hydrochloric acid at the following temperatures: 105-110, 130, 145, 160, 180 and 200°.

The results are shown in Table 2.

b) Effect of concentration of hydrochloric acid upon 2-benzyl-5-amino-benzimidazole yield. Equimolecular quantities of 1,2,4-triaminobenzene chloride (1.96 g) and phenylacetic acid (1.36 g) were heated for 7 hours under pressure in a sealed tube to 150-160° in the presence of various concentrations of hydrochloric acid.

Table 3 shows the experimental results.

c) Effect of duration of heating upon 2-benzyl-5-amino-benzimidazole yield. Equimolecular quantities of 1,2,4-triaminobenzene chloride (1.96 g) and phenylacetic acid (1.36 g) were heated for various periods of time in a sealed tube under pressure in the presence of 35% hydrochloric acid.

Table 4 shows the experimental results.

The following gave the best yields of 2-benzyl-5-amino-benzimidazole dichloride: equimolecular quantities of 1,2,4-triaminobenzene hydrochloride (1.96 g) and phenylacetic acid (1.36 g) were heated for 7 hours in a tube under pressure in the presence of 10 ml concentrated hydrochloric acid. The tube contents were extracted by means of 150 ml water, filtered, the filtrate subjected to ether extraction to remove the phenylacetic acid and condensed to small volume in a vacuum over a water bath. After cooling the 2-benzyl-benzimidazole salt was filtered off, washed with anhydrous alcohol and ether. The average yield was 70-80%.

TABLE 2

Effect of Heating Temperature upon 2-Benzyl-5-amino-benzimidazole Chlorohydrate,(after 7 hours Heating)

No.	Heating temperature	Average yield before purification (in %)	Yield after first purification (in %)	Color of filtrate and color of substance	Remarks
1	100–110°	3–5	–	–	The initial substances were the chief products
2	120–130	71.0	64	Rose filtrate; silver-gray crystals	No contaminant dye
3	140–150	81.0	73	Rose filtrate; silver-gray crystals	Negligible quantity of black residue
4	150–160	88	79.5	Slightly bluish filtrate; silver-gray crystals	Blue dye and black residue appear
5	170–180	87.5	78.5	Blue-shaded filtrate; gray crystals	Blue dye and considerable carbon particles
6	200–210	82	74.0	Dark filtrate. Substance so dark gray as to be almost black	Much carbon and much blue dye

TABLE 3

Effect of Hydrochloric Acid Concentration Upon 2-Benzyl-5-amino-benzimidazole Yield

No.	Hydrochloric acid concentration	Yield (%)		Titration of 0.1006N $NaNO_2$	Amine content (%)	Remarks
		before purification	after purification			
1	10	60.8	54	0.296 g sub.: 12.2 ml $NaNO_2$	122	Admixture of initial triaminobenzene
2	20	62.5	57.5	0.296 g sub.: 11.3 ml $NaNO_2$	113.5	Admixture of initial triaminobenzene
3	30	71	68	0.296 g sub.: 10.3 ml $NaNO_2$	103.5	
4	35	74	72	0.296 g sub.: 10.5 ml $NaNO_2$	105.5	

TABLE 4

Effect of Duration of Heating Upon 2-Benzyl-5-amino-benzimidazole Yield (Temperature of Heating, 150-160°)

No.	Duration of heating (hrs.)	Yield (%)
1	1	63
2	3	78
3	7	79
4	12	74

0.0978 g sub.: 12 ml N_2 (21°, 766 mm). Found %: N 14.3. 0.3286 g sub.: 22.0 ml 0.1020 N NaOH. 0.2960 g sub.: 19.7 ml 0.1020 N NaOH. 0.2364 g sub.: 15.66 ml 0.1020 N NaOH. $C_{14}H_{13}N_3 \cdot 2HCl$. Calculated %: N 14.18; ml 0.102 N NaOH: 21.8, 19.6, 15.6. 0.2711 g sub.: 9.2 ml 0.0945 N $NaNO_2$. Found %: amine content 100.35.

The silver-gray needles, melting and decomposing at 280-285°, were readily soluble in water (14 g in 100 ml water), and slightly in 96% alcohol, readily diazotized, and the diazo compounds combined with Azotol A to form a crimson dye.

Decomposition followed long-term heating in hydrochloric acid. Aqueous solutions were acidic:

The pH of an 0.5% solution was 3.0-3.1, 1.0% – 2.8 - 2.9, 3.0% – 2.6 - 2.7. The basicity constant was $10^{-7.7}$. The potentiometric titration curve showed two points of inflexion.

The picrate was yellow in color, and its melting point was 220-221°, at which deomposition occurred.

The ash content of the substance attained 0.3-0.5%.

2-(β-Phenyl-ethyl.-5-amino-benzimidazole dichloride

This salt was obtained by heating equimolecular quantities (0.01 mole) of 1,2,4-triaminobenzene hydrochloride and phenylacetic acid to 150-160° for 7 hours in a sealed tube under pressure in the presence of 10 ml concentrated hydrochloric acid. The tube contents were processed as above. The yield was 2.2, 2.3, 2.1 g (about 75 %).

0.2223 g sub.: 14.0 ml 0.1020 N NaOH. 0.2235 g sub.: 14.20 ml 0.1020 N NaOH. Amine content found, %: 99.5, 100.5. 0.1002 g sub.: 12.0 ml N_2 (22°, 770 mm). Found %: N 13.7. $C_{15}H_{15}N_3 \cdot 2HCl$. Calculated %: N 13.54.

These light gray flakes, which decomposed at 300°, dissolved readily in water. Aqueous solutions were acidic (0.5% solution showed a pH of 3.1-3.2). The coefficient of basicity was $10^{-7.2}$. There were two points of inflexion in the potentiometric titration curve.

2-Phenyl-5-amino-benzimidazole dichloride

This salt was obtained by reacting 1.96 g 1,2,4-triaminobenzene chlorohydrate with 1.22 g benzoic acid in the presence of 10 ml concentrated hydrochloric acid while heating to 150-160° for 7 hours under pressure.

The reaction of this acid with 1,2,4-triaminobenzene proceeded less satisfactorily than its condensation with phenylacetic and hydrocinnamic acids. The product was dirty. It did not prove possible to free this product of its contaminants completely. The yield was about 10-15%.

0.2525 g sub.: 8.6 ml 0.1006 N $NaNO_2$. Amine content found, %: 98.0.

Reaction of certain o-phenylenediamine dichloride derivatives with phenylacetic acid

Condensation of o-phenylenediamine dichlorides with 3,4-toluylenediamine, 3,4-diamino-chlorobenzene and 1,2,4-triaminobenzene with phenylacetic acid was performed as above. The data derived are presented in Table 5.

TABLE 5

Dependence of 2-Benzyl-benzimidazole Derivatives upon the Basicity of the Ortho-diamine

No.	Benzimidazole derivative	o-Diamine (salt)	Basicity of o-Diamine	Yield,%
1	2-Benzyl-5-chloro-benzimidazole	3,4-Diamino-chloro-benzene	pH 4.3 $K10^{-9.7}$	95*
2	2-Benzyl-benzimidazole	o-Phenylenediamine	pH 4.85 $K10^{-9.15}$	89
3	2-Benzyl-5-methyl-benzimidazole	3,4-Toluylenediamine	pH 5.0 $K10^{-9.0}$	68
4	2-Benzyl-5-amino-benzimidazole	1,2,4-Triaminobenzene	pH 6.1 $K10^{-7.9}$	77

2-Benzyl-5-Chlorobenzimidazole dichloride

2-Benzyl-5-chlorobenzimidazole, a base, was obtained in yield of about 95% (before purification). Melting point 171-172° (from aqueous alcohol). This base was very slightly soluble in water, but dissolved readily in alcohol. The 2-benzyl-5-chlorobenzimidazole hydrochloride was isolated by saturating an alcohol solution of the base with hydrogen chloride. The resultant small white needles, having a melting point of 248-250°, were very slightly soluble in cold water, but dissolved in alcohol.

0.2058 g sub.: 0.1051 g AgCl. 0.1831 g sub.: 0.0953 g AgCl. Found %: Cl 12.81, 12.90. $C_{14}H_{11}N_2Cl \cdot HCl$. Calculated %: Cl 12.70.

The 2-benzyl-benzimidazole and 2-benzyl-5-methylbenzimidazole dichlorides showed properties corresponding to those described in the literature [3,4].

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* From 0.01 mole o-diamine and 0.01 mole phenylacetic acid.

SUMMARY

1. The concentration of hydrochloric acid, the temperature and duration of heating strongly affect reaction of ortho-diamines with carboxylic acids in the presence of hydrochloric acid.

2. The fact was confirmed that in certain instances the less basic o-phenylenediamine derivatives provide a higher benzimidazole yield in the presence of hydrochloric acid than do the more basic. It was determined that 1,2,4-triaminobenzene is an exception to this rule among the substances studied.

3. It was established that 1,2,4-triaminobenzene reacts with benzoic, hydrocinnamic and phenylacetic acids in the presence of concentrated hydrochloric acid to form 2-phenyl,2-benzyl- and 2-(β-phenyl-ethyl)-5-amino-benzimidazole. The latter two compounds were produced for the first time.

4. Optimum conditions for the synthesis of certain 5-amino-benzimidazole derivatives were found.

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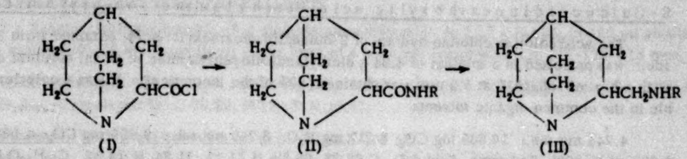
* See Consultants Bureau English translation, page 1555.

SYNTHESIS OF SUBSTITUTED 2-AMINOMETHYLQUINUCLIDINES

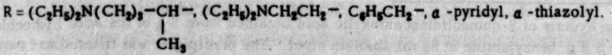
M. V. Rubtsov and E. S. Nikitskaya

A previous communication [1] described the process of obtaining aminoalkyl derivatives of quinuclidine



(I) (II) (III)

Application of this process made possible the synthesis, described in this article, of the series of compounds having (III) as their general formula, where

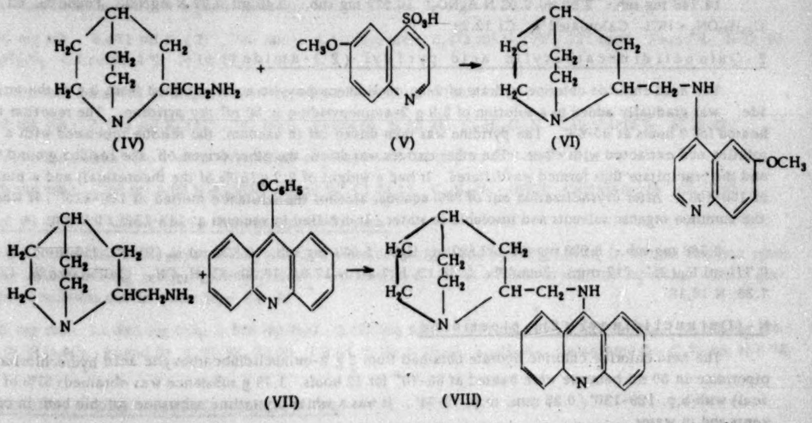


$R = (C_2H_5)_2N(CH_2)_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-,\ (C_2H_5)_2NCH_2CH_2-,\ C_6H_5CH_2-,\ \alpha\text{-pyridyl},\ \alpha\text{-thiazolyl}.$

The amides (II) were obtained in an ether, benzene or pyridine medium, and they were reduced with lithium aluminum hydride in a medium of ether or ether mixed with benzene.

Attempts to obtain quinoline and acridine derivatives by an analogous procedure did not prove successful. Under the conditions described, 6-methoxy-4-aminoquinoline and 9-aminoacridine do not react with the acid chloride of 2-quinuclidinecarboxylic acid. Nor did it prove possible to obtain compound (VI) by reacting 2-aminomethylquinuclidine with 6-methoxy-4-chloroquinoline.

2-Aminomethylquinuclidine derivatives, containing the quinoline and acridine rings, were obtained by reacting 2-aminomethylquinuclidine [1] with 6-methoxy-4-sulfoquinoline and 9-phenoxyacridine as follows:



(IV) (V) (VI)

(VII) (VIII)

Reaction of 2-aminomethylquinuclidine with 6-methoxy-4-sulfoquinoline proceeds in an aqueous medium, while reaction with 9-phenoxyacridine proceeds in n-butyl alcohol.

EXPERIMENTAL

2-Quinuclidinecarboxylic acid diethylaminoethylamide

The acid chloride chlorine hydrate obtained as previously indicated [1] from 3 g 2-quinuclidinecarboxylic acid hydrochloride was processed in a solution of 5.45 g diethylaminoethylamine in 80 ml absolute ether and permitted to stand for 2 hours. 3 g substance (77%) was obtained with a b.p. of 170 to 180° at 7 mm.

It was a colorless oily liquid, readily soluble in the common organic solvents.

3.234 mg sub: 7.818 mg CO_2; 3.139 mg H_2O. 6.750 mg sub.: 0.989 ml N_2 (23°, 732 mm). Found %: C 65.97; H 10.86; N 16.28. $C_{14}H_{27}ON_3$. Calculated %: C 66.40; H 10.67; N 16.60.

2-Quinuclidinecarboxylic acid diethylaminoisopentylamide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid, obtained from 3 g of the acid hydrochloride, was processed in a solution of 4.94 g diethylaminoisopentylamine in 80 ml absolute ether. 3.6 g of a substance with a b.p. of 150-151° at 0.3 mm was obtained (80% of the theoretical). It was a colorless oily liquid, readily soluble in the common organic solvents.

4.244 mg sub.: 10.635 mg CO_2; 4.217 mg H_2O. 3.990 mg sub.: 9.990 mg CO_2; 4.008 mg H_2O. 4.937 mg sub.: 0.628 ml N_2 (23°, 742 mm). Found %: C 68.38, 68.33; H 11.11, 11.24; N 14.32. $C_{17}H_{33}O_3N_3$. Calculated %: C 68.47; H 11.17; N 14.23.

2-Quinuclidinecarboxylic acid benzylamide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid obtained from 3 g of the acid hydrochloride was added to a solution of 5.2 g benzylamine in 80 ml absolute ether. The precipitate was filtered and carefully washed in chloroform. The chloroform-and-ether extract was stirred with 50 ml of a 50% potash solution, dried with calcined potash and the solvent driven off. 2.36 g of a substance with a b.p. of 183-185° at 0.2 mm was obtained (62.6% of the theoretical). A colorless, immobile liquid, dissolving readily in the common organic solvents, but with difficulty in water.

3.472 mg sub.: 9.330 mg CO_2; 2.630 mg H_2O. 4.040 mg sub.: 0.425 ml N_2 (29°, 729 mm). Found %: C 73.33; H 8.47; N 11.39. $C_{15}H_{20}ON_2$. Calculated %: C 73.77; H 8.19; N 11.47.

The hydrochloride was a white crystalline substance with m.p. 166-168°, readily soluble in alcohol and water, but insoluble in ether.

14.746 mg sub.: 2.60 ml 0.02 N $AgNO_3$. 14.579 mg sub.: 2.49 ml 0.02 N $AgNO_3$. Found %: Cl 12.50, 12.11. $C_{15}H_{20}ON_2 \cdot HCl$. Calculated %: Cl 12.29.

2-Quinuclidinecarboxylic acid pyridyl-(2')-amide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid, obtained from 3 g of the acid hydrochloride, was gradually added to a solution of 5.9 g 2-aminopyridine in 50 ml dry pyridine. The reaction mixture was heated for 3 hours at 60-65°. The pyridine was then driven off in vacuum, the residue processed with a 50% potash solution and extracted with ether. The ether extract was dried, the ether driven off, the residue ground with water, and the precipitate thus formed was filtered. It had a weight of 2.2 g (61% of the theoretical) and a melting point of 106-108°. After crystallization out of 33% aqueous alcohol the substance melted at 109-110°. It was soluble in the common organic solvents and insoluble in water. It distilled in vacuum at 149-150° / 0.3 mm.

3.580 mg sub.: 8.938 mg CO_2; 2.527 mg H_2O. 5.058 mg sub.: 0.824 ml N_2 (21.5°, 715 mm). 4.490 mg sub.: 0.771 ml N_2 (25°, 717 mm). Found %: C 68.13; H 7.58; N 17.81, 18.56. $C_{13}H_{17}ON_3$. Calculated %: C 67.53; H 7.35; N 18.18.

N-[Quinuclidinoyl-(2)]-piperidine

The acid chloride chlorine hydrate obtained from 3 g 2-quinuclidinecarboxylic acid hydrochloride, and 4 g piperidine in 50 ml benzene were heated at 60-70° for 12 hours. 1.79 g substance was obtained (51% of the theoretical) with b.p. 129-130° / 0.35 mm, m.p. 72-74°. It was a white crystalline substance soluble both in organic solvents and in water.

4.170 mg sub.: 10.740 mg CO_2; 3.698 mg H_2O. 3.469 mg sub.: 8.917 mg CO_2; 3.071 mg H_2O. 7.198 mg sub.: 0.800 ml N_2 (26°, 729 mm). 7.940 mg sub.: 0.902 ml N_2 (28.5°, 730 mm). Found %: C 70.28, 70.15; H 9.92, 9.91; N 12.17, 12.36. $C_{13}H_{22}ON_2$. Calculated %: C 70.27; H 9.90; N 12.61.

2-Quinuclidinecarboxylic acid thiazolyl-(2')-amide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid obtained from 3 g of the acid, was added to a solution of 4.7 g 2-amino-thiazole in 50 ml pyridine, and the reaction mixture was heated for 8 hours at 60-70°. Upon cooling, the precipitate deposited was filtered, dissolved in 10 ml water, to which a 50% potash solution was added until an alkaline reaction was obtained with phenolphthalein. The precipitate obtained was filtered, washed with water and recrystallized from the water. It was a white crystalline substance, soluble in organic solvents and in boiling water. The m.p. was 114-116°. The yield was 2.1 g (57% of the theoretical).

3.256 mg sub.: 6.667 mg CO_2; 1.809 mg H_2O. 4.860 mg sub.: 0.796 ml N_2 (25°, 731 mm). Found %: C 55.87; H 6.22; N 18.05. $C_{11}H_{15}ON_3S$. Calculated %: C 56.11; H 6.32; N 17.76.

2-Diethylaminoethylaminomethylquinuclidine

Reduction of 5.07 g 2-quinuclidinecarboxylic acid diethylaminoethylamide by 1.52 g $LiAlH_4$ in 100 ml absolute ether gave 3.2 g of the amine (70% of the theoretical) in the form of a colorless liquid with b.p. 171-173° / 13 mm.

3.105 mg sub.: 7.923 mg CO_2; 3.280 mg H_2O. 3.672 mg sub.: 0.582 ml N_2 (27°, 739 mm). Found %: C 69.63; H 11.84; N 17.53. $C_{14}H_{29}N_3$. Calculated %: C 70.29; H 12.13; N 17.57.

The tripicrate consisted of yellow crystals with an m.p. of 164.5-166.5°.

3.279 mg sub.: 0.549 ml N_2 (28.5°, 727 mm). 4.890 mg sub.: 0.799 ml N_2 (29°, 733 mm). Found %: N 18.15; 17.79. $C_{32}H_{38}O_{21}N_{12}$. Calculated %: N 18.14.

2-Diethylaminoisopentylaminomethylquinuclidine

Reduction of 2.9 g 2-quinuclidinecarboxylic acid diethylaminoisopentylamide by 0.45 g $LiAlH_4$ in 80 ml absolute ether produced 2 g of the amine (72% of the theoretical) in the form of a colorless oily liquid with b.p. 144-146° at 0.2 mm, soluble both in organic solvents and water.

The triphosphate was a white crystalline hygroscopic substance.

4.702 mg sub.: 6.090 mg CO_2; 3.167 mg H_2O. Found %: C 35.35; H 7.54. $C_{17}H_{35}N_3 \cdot 3H_3PO_4$. Calculated %: C 35.47; H 7.65.

2-Benzylaminomethylquinuclidine

4.27 g 2-quinuclidinecarboxylic acid benzylamide was reduced by 1 g $LiAlH_4$ in 100 ml of an ether-benzene mixture (1 : 1). 2.94 g of a substance with b.p. 191° at 0.25 mm was obtained (73% of the theoretical). It was a colorless viscous liquid soluble in organic solvents.

4.380 mg sub.: 0.471 ml N_2 (27°, 739 mm). 4.440 mg sub.: 0.473 ml N_2 (22°, 727 mm). Found %: N 11.89, 11.80. $C_{15}H_{22}N_2$. Calculated %: N 12.17.

The dipicrate consisted of bright yellow crystals with m.p. 190-191°.

5.107 mg sub.: 0.755 ml N_2 (31°, 731 mm). Found %: N 15.95. $C_{27}H_{28}O_{14}N$. Calculated %: N 16.27.

The dihydrochloride was a white crystalline substance with an m.p. of 202-204°.

9.275 mg sub.: 2.99 ml 0.02 N $AgNO_3$. Found %: Cl 23.11. $C_{15}H_{22}N_2 \cdot 2HCl$. Calculated %: Cl 23.43.

2-[Pyridyl-(2')]-aminomethylquinuclidine

4.06 g 2-quinuclidinecarboxylic acid pyridyl-(2')-amide was reduced by 0.8 g $LiAlH_4$ in 200 ml absolute ether. 2.62 g of the amine, having a b.p. of 160° / 0.25 mm was obtained. It was a white crystalline substance readily soluble in organic solvents and in water. M.p. 64 - 66°.

4.308 mg sub.: 11.363 mg CO_2; 3.325 mg H_2O. 3.323 mg sub.: 8.775 mg CO_2; 2.597 mg H_2O. 3.182 mg sub.: 4.42 ml 0.01 N H_2SO_4. Found %: C 71.98, 72.06; H 8.64, 8.76; N 19.45. $C_{13}H_{19}N_3$. Calculated %: C 71.88; H 8.75; N 19.35.

N-[Quinuclidyl-(2)-methyl]-piperidine

1.75 g N-quinuclidinoyl-(2)-piperidine was reduced by 0.6 g $LiAlH_4$ in 110 ml of absolute ether. 1.24 g of a substance with b.p. 91-93° / 0.2 mm was obtained (75.6% of the theoretical). It was a colorless liquid soluble both in organic solvents and in water.

14.343 mg sub.: 13.23 ml 0.01 N H_2SO_4. Found %: N 12.91. $C_{13}H_{24}N_2$. Calculated %: N 13.12.

The iodomethylate was a white crystalline substance readily soluble in alcohol and water; m.p. 140-142°.

6.111 mg sub.: 10.54 ml 0.01 N $Na_2S_2O_3$. Found %: I 36.50. $C_{14}H_{27}N_2I$. Calculated %: I 36.28.

2-[Thiazolyl-(2)]-aminomethylquinculidine

3.56 g 2-quinuclidinecarboxylic acid thiazolyl-(2')-amide was reduced by 0.7 g $LiAlH_4$ in 120 ml of a benzene-ether mixture (1 : 1). 2.73 g of a substance with b.p. 150-152° / 0.2 mm and m.p. 76-78° was obtained (81% of the theoretical). It was a white crystalline substance readily soluble in alcohol and acetone, poorly soluble in water.

3.716 mg sub.: 8.121 mg CO_2; 2.532 mg H_2O. 5.399 mg sub.: 7.19 ml 0.01 N H_2SO_4. 4.673 mg sub.: 6.19 ml 0.01 N H_2SO_4. Found %: C 59.64; H 7.62; N 18.65, 18.54. $C_{11}H_{17}N_3S$. Calculated %: C 59.19; H 7.62; N 18.83.

2-[6'-Methoxyquinolyl-(4')]-aminomethylquinuclidine

1.8 g 6-methoxy-4-sulfoquinoline, 2.46 g 2-aminomethylquinuclidine and 2.52 ml water were heated with stirring over a Wood bath for 16 hours at 114° (in the reaction mixture). After it had cooled, the reaction mixture was treated with 20 ml water, the white precipitate thus formed was filtered, dissolved in alcohol and then again separated from the alcohol solution by adding water to clouding. The substance obtained had an m.p. of 80-85°. It congealed at 90° and then melted at 140°. After drying the substance in vacuum at 100°, 1.51 g of substance with an m.p. of 143.5-145° was obtained (68% of the theoretical). It consisted of white crystals soluble in alcohol and ether but not in water.

3.848 mg sub.: 10.192 mg CO_2; 2.671 mg H_2O. 6.900 mg sub.: 0.853 ml N_2 (23.5°, 737 mm). Found %: C 72.28; H 7.76; N 13.83. $C_{18}H_{23}ON_3$. Calculated %: C 72.72; H 7.74; N 14.14.

The dihydrochloride was a white crystalline substance with m.p. of 280 - 282°.

7.400 mg sub.: 2.00 ml 0.02 N $AgNO_3$. 14.994 mg sub.: 4.01 ml 0.02 N $AgNO_3$. Found %: Cl 19.07, 18.97. $C_{18}H_{23}ON_3 \cdot 2HCl$. Calculated %: Cl 19.18.

2-Acridyl-(9')-aminomethylquinuclidine

3.3 g 2-aminomethylquinuclidine, 5.4 g 9-phenoxyacridine and 90 ml n-butyl alcohol were heated with boiling for 20 hours. The 1.37 g acridone produced was filtered, and the filtrate evaporated in vacuum. The residue was dissolved in 10% hydrochloric acid, the undissolved portion filtered out, the hydrochloric solution rendered colorless with charcoal and treated with a 15% solution of sodium carbonate until phenolphthalein showed an alkaline reaction. The base thus produced was ground with water in a mortar, and this gave a bright yellow crystalline substance with m.p. 144-146°. The yield was 3.97 g (63% of the theoretical). The substance was soluble in butyl alcohol upon heating, slightly soluble in ether, insoluble in water.

3.701 mg sub.: 10.761 mg CO_2; 2.352 mg H_2O. 3.473 mg sub.: 10.069 mg CO_2; 2.188 mg H_2O. Found %: C 79.35, 79.12; H 7.09, 7.05. $C_{21}H_{23}N_3$. Calculated %: C 79.49; H 7.25.

SUMMARY

A series of 2-alkyl (aryl) aminomethylquinuclidines was synthesized, starting with 2-quinuclidinecarboxylic acid as the initial material.

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• See Consultants Bureau English translation, page 1633.

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SYNTHESIS OF THIAZOLE DERIVATIVES

X. NITROBENZOTHIAZOLYLCARBINOLS AND THEIR CONVERSION:

V. M. Zubarovsky

A previous communication [1] described a simplified method of synthesizing benzothiazolyl-(2)-carbinol (I) and methyl-[benzothiazolyl-(2)]-carbinol (XIII). These alcohols can now be produced rapidly and in bulk. They may be regarded as readily available benzothiazole derivatives, and it now becomes possible to expand their use as raw materials for the synthesis of new compounds in this series. Certain conversions of these alcohols were effected earlier [2,3]. In the present study we investigated their nitration and the reactions of the nitrogen products thus obtained.

Nitric acid (d 1.52) was used for nitration, while the nitrated mixture was added to solutions of benzothiazolylcarbinols in concentrated sulfuric acid. Under these conditions, carbinol (I) gave a yield of 79% 6-nitrobenzothiazolyl-(2)-carbinol (II). The position of the nitryl in the new compound was demonstrated by its conversion into nitrobenzothiazole-(2)-carboxylic acid (VII), decarboxylation of which gave nitrobenzothiazole (IX), identical with the 6-nitrobenzothiazole described in the literature.

Reduction of carbinol (II) by stannic chloride resulted in the corresponding amino derivative (V).

Oxidation of carbinol (II) gives 6-nitrobenzothiazole-(2)-aldehyde (VI) and 6-nitrobenzothiazole-(2)-carboxylic acid (VII); the oxidizing agents used were selenium dioxide in the first instance, and potassium manganate in the second. We were the first to produce the aldehyde (VI) by oxidation of 2-methyl-6-nitrobenzothiazole by selenium dioxide [3]. The method of synthesizing this aldehyde set forth in the present paper must be regarded as more satisfactory than the prior method; while the nitroaldehyde yield continues to be low (30-34%), the method of synthesis is simpler and the product is considerably more pure. The pure aldehyde (VI) has an m.p. of 174°, while previously, despite the most meticulous purification, it was obtained with a 146° m.p. and a somewhat elevated nitrogen content.

The acid (VII) results from oxidation of nitrocarbinol, giving a yield of 70%, and is a colorless microcrystalline substance. The nitryl acid is purified by settling hydrochloric acid out of a warm water solution of its sodium salt. When the acid is heated in an open capillary tube it melts at 172-175°, and carbon dioxide is liberated; the acid melts at 174° without noticeable decomposition in a sealed capillary. The acid chloride (X) is obtained from its potassium salt and oxalyl chloride by the method successfully used in the synthesis of the acid chlorides of other heterocyclic acids [4]. The methyl ester (XI) and hydrazide (XII) of the nitro acid were synthesized.

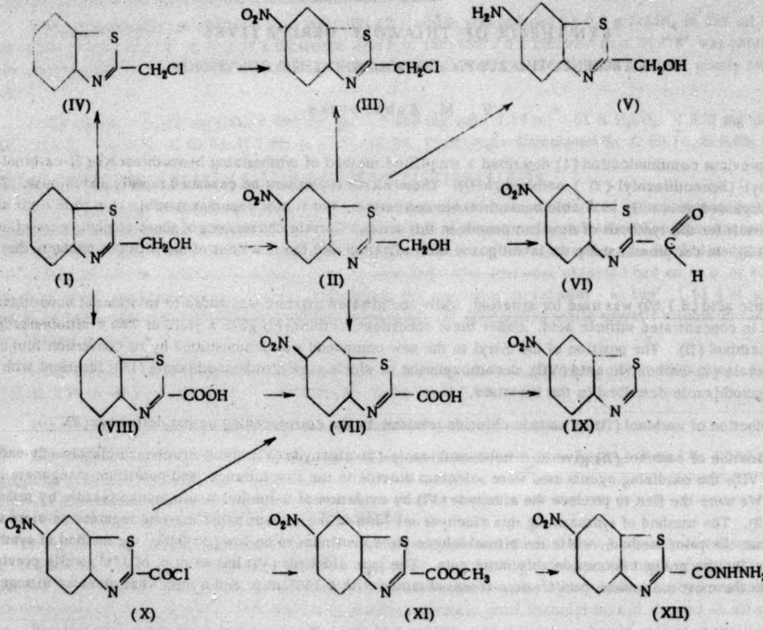
Fridman obtained acid (VII) by nitration of benzothiazole-(2)-carboxylic acid [5], while Mizuno, Adachi and Kanda recently obtained it from 2-trichloromethyl-6-nitrobenzothiazole [6]. Mizuno and associates found the acid (VII) to have an m.p. of 181-182° and do not record decarboxylation accompanying melting.

Fridman describes acid (VII) as a "light yellow amorphous powder, decomposing at 115°", while an effort to obtain its acid chloride and ester did not attain the desired ends. The divergence between our data on the properties of acid (VII) and those of Fridman caused us to undertake the nitration of benzothiazole-(2)-carboxylic acid (VIII). For this purpose we introduced a new method – oxidation of carbinol (I) by potassium permanganate. This method is simple, quick, and produces a very pure product. The methods of producing this acid described in the literature [7,8,9] are more complicated. We take this opportunity to state that the acid chloride (VIII) is readily obtained from oxalyl chloride and the potassium salt of the acid; the acid chloride thus synthesized has a melting point of 116-118°, while the literature describes it as 100° [10] and 102° [11].

Nitration of acid (VIII) produces a yellow acid, difficult to free of contaminants (VII). Crystallization of the product by decarboxylation of this acid results in a small quantity of pure 6-nitrobenzothiazole, while concentration of the mother liquor is accompanied by liberation of a product with a low boiling point (an isomer mixture, perhaps ?).

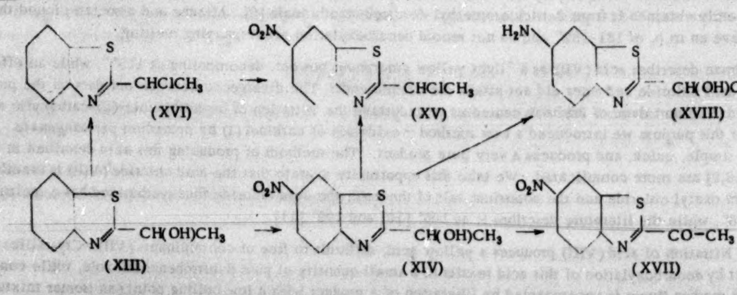
Thus, nitration of acid (VIII) as a method of synthesizing acid (VII) is not deserving of attention.

Nitration of methyl-[benzothiazolyl-(2)]-carbinol (XIII) was conducted in a manner analogous to nitration of carbinol (I).



The nitration product, methyl-[6-nitrobenzothiazolyl-(2)]-carbinol (XIV) was subjected to the same conversions as its analog – carbinol (II).

These conversions gave: the oxidation product, methyl-[6-nitrobenzothiazolyl-(2)]-ketone (XVII), the reduction product, methyl-[6-amino-benzothiazolyl-(2)]-carbinol (XVIII) and the chlorine-for-alcohol-group substitution product – 6-nitro-2-(α -chloroethyl)-benzothiazole (XV). The latter also results from the nitration of 2-(α -chloroethyl)-benzothiazole (XVI).



The ketone (XVII) was oxidized by potassium permanganate into the acid (VII), from which 6-nitrobenzothiazole (IX) was obtained, this being the means by which the structure of all the nitro and amino derivatives synthesized from carbinol (XIII) was determined.

EXPERIMENTAL

1. 6-Nitrobenzothiazolyl-(2)-carbinol (II). Benzothiazolyl-(2)-carbinol, twice recrystallized from toluol, was chosen for nitration. The carbinol (24.75 g; 0.15 mole) was dissolved in 20 ml concentrated sulfuric acid. To accomplish this, carbinol was added, bit by bit, to sulfuric acid in a porcelain mortar, and after each addition, the mixture was ground until the formation of a solution in which a cloudy appearance was not objectionable, but in which a noticeable yellow color was impermissible as this was a sign that the carbinol was not pure enough.

The thick, viscous solution was transferred to a reaction vessel with stirrer, thermometer and dropping funnel, where it was nitrated with a mixture consisting of 14.25 g (9.4 ml; 0.225 mole) nitric acid (d 1.52) and 15 ml concentrated sulfuric acid. The reaction vessel was placed in a bath containing a coolant mixture, and the nitrating mixture was added over a period of 30 minutes at a temperature (in the reaction mixture) not exceeding 10°. When the addition was completed, the ice bath was removed and stirring continued until the temperature rise due to exothermic reaction ceased. The reaction vessel was then placed in a warm water bath and a 60° temperature was maintained within the reaction vessel for an hour and a half, upon which heating was brought to an end and the mixture set aside for 15 hours. The mixture was then poured into 400 ml of water containing pieces of ice, the yellow-white precipitate filtered off, washed by suspension with 100 ml of a 10% aqueous sodium carbonate solution, 100 ml of a 10% hydrochloric acid solution, and water. The yield of dry nitro product was 25 g (79.3% of the theoretical).

After crystallization from 80 ml ethyl alcohol (1 g per 4 ml, charcoal being used), 14 g nitrocarbinol in the form of thin yellow white needles with a melting point of 153° was obtained. The colorless nitrocarbinol was obtained upon recrystallization from a mixture of water and acetone (1 : 1) and then had an m.p. of 165°.*

Found %: S 15.52, 15.58. $C_8H_6O_3N_2S$. Calculated %: S 15.24.

2. 2-Chloromethyl-benzothiazole (IV). 4.95 g (0.03 mole) benzothiazolyl-(2)-carbinol and 6.9 g (0.033 mole) phosphorous pentachloride, both pulverized, were rapidly mixed in a round-bottomed flask, which was immediately connected to a reflux condenser and placed in a coolant mixture of ice and salt. An exothermic reaction soon began, and a semi-solid brown mass was formed which was heated for 10 minutes in boiling water upon the conclusion of the exothermic reaction. Ice and then a 20% aqueous solution of sodium carbonate were added to the cooling mass until an alkaline reaction was obtained. Lumps were carefully crushed and the oily brown product extracted with ether. The extract was dried with calcium chloride, the solvent driven off and the residue vacuum-distilled. A fraction with a b.p. of 110° / 2 mm was collected. The yield was 3.0 g (54.5% of the theoretical). It was a colorless oil, crystallizing as it cooled. The chloride was recrystallized from petroleum ether (the solution was shaken up with charcoal, concentrated and cooled with ice) and obtained in the form of colorless crystals with an m.p. of 34°.

Found %: N 7.55, 7.58. C_8H_6NSCl. Calculated %: N 7.63.

3. 6-Nitro-2-chloromethyl-benzothiazole (III). A. From 6-nitrobenzothiazolyl-(2)-carbinol. 3.15 g (0.015 mole) 6-nitrobenzothiazolyl-(2)-carbinol and 3.12 g (0.015 mole) phosphorous pentachloride were used in this synthesis. The method did not differ in any respect from that of the preceding experiment, No. 2. Addition of the sodium carbonate solution produced a precipitate, which was filtered out, washed with water, desiccated and recrystallized (carbon) from ligroin (with a b.p. of 100-120°). The yield of substance, once recrystallized, was 1.5 g (43% of the theoretical); the product consisted of colorless crystals with an m.p. of 101°. Recrystallization from ligroin gave 6-nitro-2-chloromethylbenzothiazole with an m.p. of 105°.

Found %: N 11.95, 12.15. $C_8H_5O_2N_2SCl$. Calculated %: N 12.26.

B. From 2-chloromethyl-benzothiazole. 1.84 g (0.01 mole) of 2-chloromethyl-benzothiazole was dissolved in 2 ml concentrated sulfuric acid and nitrated with a mixture of 0.95 g (0.015 mole) nitric acid (d 1.52) and 1 ml concentrated sulfuric acid. The conditions of nitration were described above under Experiment 1. The nitrated mixture was poured onto ice; the viscous substance resulting soon solidified. It was washed in a sodium carbonate solution and in water, and recrystallized from 30 ml ligroin (charcoal used).

The yield of recrystallized substance was 1.0 g (43.5% of the theoretical). 6-Nitro-2-chloromethyl-benzothiazole twice recrystallized from ligroin had an m.p. of 103°, and a mixture thereof with the same compound, obtained by method A, melted at 103-104°.

4. 6-Aminobenzothiazolyl-(2)-carbinol (V). 2.1 g (0.01 mole) 6-nitrobenzothiazolyl-(2)-carbinol was added, bit by bit, with stirring, to 7.3 g (0.033 mole) stannic chloride dissolved in 8.2 ml concentrated hydrochloric acid, heated to 75°. Each addition resulted in the appearance of an orange coloration which disappeared with stirring. The mixture was heated for an hour in a boiling water bath and left for 12 hours, upon which ice and a 20% solution of

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* Corrected melting and boiling temperatures are used throughout for the substances undergoing analysis.

caustic soda were added until the white stannic hydroxide precipitate disappeared. The yellow crystalline aminobenzothiazolyl carbinol precipitate was filtered out and repeatedly washed in a 2% aqueous sodium hydroxide solution. The yield of aminocarbinol was 1.0 g (55% of the theoretical). After single distillation from xylol (with use of charcoal), the aminocarbinol was obtained in the form of small yellow-white crystals with an m.p. of 151°. 6-Aminobenzothiazolyl-(2)-carbinol is readily soluble without heating in dilute hydrochloric acid (1 : 5), ethyl alcohol and dioxan; it can be diazotized, and its diazocompounds combine with β-naphthol to form an orange-yellow dye.

Found %: N 15.91; S 17.62, 17.45. $C_8H_8ON_2S$. Calculated %: N 15.56; S 17.77.

5. 6-Nitrobenzothiazole-(2)-aldehyde (VI). A warm solution of 6.65 g (0.06 mole) selenium dioxide in 30 ml dioxan and 3 ml water was added suddenly to 10.5 g (0.05 mole) 6-nitrobenzothiazolyl-(2)-carbinol. The mixture was heated with uninterrupted mixing to rapid boiling, and boiled two hours. The selenium precipitate was filtered off and the filtrate poured into 250 ml water. The yellow product liberated was filtered*, washed in water and, while moist, twice crystallized from an acetone-water mixture (5 : 4), while the portion that failed to dissolve in hot aqueous acetone was discarded. The mother liquors were decolorized with a considerable amount of charcoal, and were cooled for a long period with ice. The nitroaldehyde yield was 3.5 g (33.6% of the theoretical) the m.p. 169°. After two further crystallizations from ethyl alcohol (10% charcoal) the aldehyde was obtained as colorless, odorless crystals with m.p. 174°.

Found %: N 13.38, 13.40. $C_8H_4O_3N_2S$. Calculated %: N 13.46.

The nitroaldehyde thiosemicarbazone, recrystallized from glycol, had a decomposition temperature of 287-289°. It was also prepared by oxidizing 6-nitro-2-methyl-benzothiazole [3]; after crystallization from glycol its decomposition temperature was 287°, and a mixture of the two thiosemicarbazone samples decomposed at 287° when heated in a capillary tube.

6. 6-Nitrobenzothiazole-(2)-carboxylic acid (VII). This synthesis was performed on the basis of 6-nitrobenzothiazolyl-(2)-carbinol, twice recrystallized, once from ethyl alcohol and once from aqueous acetone. 10.5 g (0.05 mole) of this compound was introduced into 2 liters of hot water, and the suspension heated to active boiling, at which point a yellow solution was formed. Heating was suspended, and when the temperature dropped to 90°, a warm solution of 7.9 g (0.05 mole) potassium permanganate in 500 ml water was added. Mixing continued, and within 7 minutes the manganese dioxide precipitate was filtered off and washed in a small quantity of boiling water. 10 ml concentrated hydrochloric acid was added to the warm filtrate, with stirring, and the white precipitate was filtered, washed in water and air dried. The nitro acid yield was 7.85 g (70% of the theoretical).

The acid was converted to a sodium salt, and the latter precipitated out of a warm aqueous solution by hydrochloric acid. After air drying the acid had a b.p. of 165-171°, at which decomposition occurred. When the acid was heat dried, partial decarboxylation occurred, and analysis showed an elevated nitrogen content. Air and desiccator drying, however, went slowly. The sodium salt of the acid, obtained by dissolving the acid in a warm water solution of sodium carbonate with subsequent cooling of the solution obtained, was subjected to analysis. The salt was twice recrystallized out of water (the mother liquors having been shaken with charcoal) and obtained in the form of colorless crystals with a pearl-like luster, having a decomposition temperature of 335°. The salt contained water of crystallization, readily discovered in the usual manner, which was lost uponupon vacuum drying at 135°. Prior to the drying of the salt:

Found %: N 10.54, 10.53. $C_8H_3O_4N_2SNa \cdot H_2O$. Calculated %: N 10.60.

After drying:

Found %: N 11.26. $C_8H_3O_4N_2SNa$. Calculated %: N 11.38.

The nitro acid, isolated from the pure twice recrystallized sodium salt, washed in alcohol and ether, and dried in a vacuum desiccator, melted in an open capillary at 172-175° with liberation of carbon dioxide, and in a closed capillary at 174° without noticeable decomposition.

To obtain the potassium salt of the acid, 2.4 g (0.0175 mole) of potassium carbonate was dissolved in 60 ml water, and 7.85 g (0.035 mole) 6-nitrobenzothiazole-(2)-carboxylic acid was added, bit by bit, with stirring, to the solution, heated to 70-75°. During the addition it was necessary to make sure that the potassium salt did not crystallize, and to heat the solution when a precipitate appeared. The precipitate was shaken with charcoal, filtered and ice cooled. The crystallized salt was filtered, ground with alcohol in a mortar, again filtered, washed in alcohol until a colorless filtrate appeared, and then in ether. The yield was 7 g, and the decomposition temperature, 268°.

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* In repetitions of the experiment, filtration of this precipitate sometimes proved difficult; when this occurred it was necessary to add a few milliliters of a saturated sodium chloride solution to the suspension.

7. Decarboxylation of 6-nitrobenzothiazole-(2)-carboxylic acid. 0.9 g 6-nitrobenzothiazole-(2)-carboxylic acid was heated in a test tube in an air bath until liberation of carbon dioxide ceased. The test tube residue, which solidified upon cooling, was recrystallized (with the aid of charcoal) from ethyl alcohol. After being cooled with ice, the pale-yellow crystalline precipitate (IX) was filtered, and weighed after drying 0.6 g (85.7% of the theoretical); the m.p. was 174°. The m.p. of a mixture of this decarboxylation product (1: 1) with known 6-nitrobenzothiazole (m.p. 173-174° [12]) was 174°.

8. 6-Nitrobenzothiazole-(2)-carboxylic acid chloride. (X). The potassium salt of 6-nitrobenzothiazole-(2)-carboxylic acid was dried for 3 hours at 110-130°, and then in a vacuum desiccator over sulfuric acid. A solution of 3.2 g (0.025 mole) oxalyl chloride in 10 ml dry benzene was added, drop by drop, with stirring, to an ice-cooled suspension of 6.55 g (0.025 mole) fine powder of the salt in 25 ml dry benzene. The addition was performed at a rate that prevented noticeable evolution of heat by the mixture, and, in any case, so that its temperature would not exceed 10°. When addition was completed, mixing continued for another 15 minutes, upon which the bath containing ice was replaced by a cold water bath, whereupon the latter, after half an hour, was slowly warmed to the point at which, after 25-30 minutes, it reached the boiling point; it was then kept boiling for another 30 minutes. The hot contents of the reaction vessel were filtered, the filtrate cooled in ice for an hour, the orange acid chloride precipitate filtered and washed with petroleum ether. The yield was 2.5 g (31%). The acid chloride was heated with 30 ml dry benzene, the insoluble portion discarded, and the solution, after shaking with charcoal and filtration, was concentrated and cooled. The pure acid chloride was a pale-yellow fine crystalline powder with an m.p. of 138°.

Found %: N 11.39. $C_8H_3O_3N_2SCl$. Calculated %: N 11.55.

The acid chloride reacts violently with ammonia in aqueous solution, forming 6-nitrobenzothiazole-(2)-carboxylic acid amide, consisting of colorless fine crystals with an m.p. of 280° (butyl alcohol).

9. 6-Nitrobenzothiazole-(2)-carboxylic acid methyl ester (XI). A mixture of 2.0 g 6-nitrobenzothiazole-(2)-carboxylic acid chloride and 30 ml anhydrous methyl alcohol was boiled for two hours and then set aside for 15 hours. The precipitate was filtered and recrystallized from methyl alcohol (with the aid of charcoal). The yield was 1.0 g (51% of the theoretical); m.p. 178°. After double crystallization with charcoal from a mixture (12 ml mixture to 1 g ether) of dioxan and ethyl alcohol (1 : 2), the 6-nitrobenzothiazole-(2)-carboxylic acid methyl ester appeared in the form of fine colorless needles, m.p. 179°.

Found %: N 11.97. $C_9H_6O_4N_2S$. Calculated %: N 11.76.

6-Nitrobenzothiazole-(2)-carboxylic acid ethyl ester is obtained similarly to the production of the ethyl alcohol acid chloride. It consists of colorless needles with m.p. 182° (from ethyl alcohol).

10. 6-Nitrobenzothiazole-(2)-carboxylic acid hydrazide (XII). 1.95 g (0.04 mole) of hydrazine hydrate dissolved in 6 ml alcohol was added, with stirring, to 1.2 g (0.005 mole) 6-nitrobenzothiazole-(2)-carboxylic acid methyl ester suspended in 15 ml ethyl alcohol. The mixture was heated for half an hour in boiling water, whereupon it was cooled in ice, and the bright, fine crystalline precipitate was filtered and washed on the filter with alcohol diluted with water (1 : 1) until the draining filtrate was no more than faintly yellow; the precipitate was then washed with alcohol and ether. Yield 0.9 g (75%). The hydrazide was purified by crystallization from an ample mixture of ethyl alcohol and water (3 : 2), and the solution was decolorized with alcohol. Slow cooling was accompanied by the appearance of fine light-yellow needles, which were filtered off and washed in alcohol and ether. The hydrazide melted, with decomposition, at 215-217°.

Found %: N 23.38, 23.70. $C_8H_6O_3N_4S$. Calculated %: N 23.53.

11. Benzothiazole-(2)-carboxylic acid (VIII). Benzothiazole-(2)-carbinol, recrystallized from toluol, was used. 33 g (0.2 mole) benzothiazole-(2)-carbinol, pulverized, was added, with stirring, to 2 liters water, heated to 80°; the solution was quickly filtered. 31.6 g (0.2 mole) potassium permanganate in 250 ml hot water was added (in 5 to 10 min), with stirring, to the hot filtrate (75°). Without further heating, stirring was continued for another 5 minutes, the MnO_2 filtered off, and the acid extracted with a small quantity of boiling water. The filtrate was allowed to cool to 35°, then 40 ml concentrated HCl was added all at once. The suspension was cooled by ice, and the fine, white crystalline benzothiazole-(2)-carboxylic acid precipitate was filtered and washed on the filter with cold water, then with ether. 22 g acid (61% of the theoretical); m.p. 106-108°, (decomp.) (literature data m.p. 108°, with decomp. [7]). The acid potassium salt resulted from equivalent amounts of the acid and potash. 26.85 g (0.15 mole) of the acid was added to warm solution of 10.35 g (0.075 mole) potash in 185 ml water, the mixture was heated to complete solution of the precipitate, the solution allowed to cool and then cooled with ice. Crystallized salt was filtered off and washed with ether. Yield 21.8 g, m.p. 370° (decomp.). Evaporation of the mother liquor over a water bath provided additional quantities of the salt.

Benzothiazole-(2)-carboxylic acid chloride was obtained in the same manner as 6-nitrobenzothiazole-(2)-carboxylic acid chloride (experiment No. 8). The benzothiazole-(2)-carboxylic acid potassium salt was dried at 125° and then in a vacuum desiccator over sulfuric acid. After the acid chloride was filtered out of the cooled benzene solution, the bulk of the solvent was distilled off the filtrate and more of the acid chloride was obtained from the concentrate. 5.0 g (63.2%) acid chloride was obtained from 8.7 g (0.04 mole) benzothiazole-(2)-carboxylic acid potassium salt and 5.0 g (0.04 mole) oxalyl chloride. The crude acid chloride, comprising pale yellow needles, had an m.p. of 115°. After double crystallization (with charcoal) from petroleum ether, the acid chloride was obtained in the form of yellow-white crystals, m.p. 116-118°.

Found %: N 7.15, 7.12. C_8H_4ONSCl. Calculated %: N 7.09.

12. Nitration of benzothiazole-(2)-carboxylic acid. 5.9 g (0.033 mole) benzothiazole-(2)-carboxylic acid was dissolved in 10 ml concentrated sulfuric acid, and the thick yellow solution thus formed was nitrated with a mixture consisting of 3.15 g (0.05 mole) nitric acid (d 1.52) and 3.5 ml concentrated sulfuric acid. The method of nitration was the same as that used in Experiment No. 1 for the synthesis of 6-nitrobenzothiazole-(2)-carbinol. After the nitrated mixture had been poured into 150 ml water containing ice, the yellow precipitate was filtered, washed in water and heated (50°) when moist with a solution of 3.0 g potash in 75 ml water. The solution was partially decolorized by charcoal and acidified with hydrochloric acid. The nitro acid thus evolved was filtered, washed with water and air dried. The yield was 5.5 g, m.p. 115-117°.

1.0 g nitro acid was subjected to decarboxylation. The product thus formed was crystallized from 14 ml ethyl alcohol (with use of charcoal). 0.3 g 6-nitrobenzothiazole, m.p. 175°, was obtained. A yellow crystalline powder with m.p. 115° separated out of the mother liquor, and when crystallized from alcohol the product had an m.p. of 127°

13. Methyl-[6-nitrobenzothiazolyl-(2)-]-carbinol (XIV). The colorless carbinol obtained after double distillation of the raw carbinol from toluol (1 ml solvent to 2 g carbinol) or from a mixture of toluol (1 volume) and ligroin (1.5 volume) was used for purposes of nitration. In the latter case 3.5 ml mixture was needed for each gram carbinol. Whichever type of crystallization was used, the mother liquors were decolorized with charcoal and then cooled in ice. The nitration of methyl-[benzothiazolyl-(2)-] carbinol proceeded in a manner entirely analogous to that of benzothiazolyl-(2)-carbinol (Experiment 1). Ingredients in the following quantities were employed in the experiments: 17.9 g (0.1 mole) methyl-[benzothiazolyl-(2)]-carbinol, and 16 ml concentrated sulfuric acid to dissolve it; the nitrated mixture consisted of 9.5 g (6.25 ml; 0.15 mole) nitric acid (d 1.52) and 10 ml concentrated sulfuric acid. The product was filtered an hour after the nitrated mixture was poured into the water. The nitro product yield was 15 g (67% of the theoretical). The raw nitro product was crystallized from 85 ml ethyl alcohol (with use of charcoal). After a single crystallization the methyl-[6-nitrobenzothiazolyl-(2)]-carbinol had an m.p. of 172°. For purposes of analysis it was twice more recrystallized from ethyl alcohol and obtained as small yellow-white crystals, m.p. 176°.

Found %: N 12.57, 12.65. $C_9H_8O_3N_2S$. Calculated %: N 12.50.

14. 2-(α -Chloroethyl)-benzothiazole (XVI). The synthesis of this chloride was analogous to the synthesis of 2-chloromethyl-benzothiazole (Experiment 2). 7.15 g (0.04 mole) methyl-[benzothiazolyl-(2)-]-carbinol and 9.15 g (0.044 mole) phosphorous pentachloride were reacted. After mixing the reaction product with ice, a 20% excess of aqueous sodium hydroxide solution was added (30 ml), and the semi-solid oily chunks were carefully crushed. Fourfold ether extraction was required. Upon distillation of the raw product a fraction was obtained that boiled between 112 and 117°/3-4 mm. The yield was 5.0 g (63.2% of the theoretical). Upon redistillation the chloride boiled at 115-116°/4 mm. It was a colorless liquid with a characteristic odor, which darkened and took on a greenish fluorescence with the passage of time.

Found %: N 6.72, 6.80. C_9H_8NSCl. Calculated %: N 7.09.

15. 6-Nitro-2-(α -chloroethyl)-benzothiazole (XV). A. From methyl-[6-nitrobenzothiazolyl-(2)]-carbinol. 2.25 g (0.01 mole) methyl-[6-nitrobenzothiazolyl-(2)]-carbinol and 2.3 g (0.011 mole) phosphorous pentachloride were used. The method used was that of Experiment 3, variant A. After grinding with a sodium carbonate solution, the raw chloride was filtered, washed in water and recrystallized from ligroin (b.p. 100-120°; charcoal was used). The mother liquor was cooled with ice. Yield after one crystallization was 1.25 g (50%); m.p. 105°. When twice recrystallized, the chloride consisted of colorless crystals, m.p. 112°.

Found %: N 11.72, 11.54. $C_9H_7O_2N_2SCl$. Calculated %: N 11.55.

B. From 2-(α -chloroethyl)-benzothiazole. 1.98 g (0.01 mole) 2-(α -chloroethyl)-benzothiazole, dissolved in 2 ml concentrated sulfuric acid, was nitrated as in Experiment 3, variant B. The nitration mixture consisted of 0.95 g

(0.015 mole) nitric acid (d 1.52) and 1 ml concentrated sulfuric acid. The nitro product was crystallized out of ligroin. Yield 1.2 g (50% of the theoretical). The nitro product m.p. was 112° and a mixture thereof with the product obtained by the previous variant, A, of the present experiment, melted at 112°.

16. Methyl-[6-aminobenzothiazolyl-(2)]-carbinol (XVIII). Reduction of methyl-[6-nitrobenzothiazolyl-(2)]-carbinol followed exactly the same lines as reduction of 6-nitrobenzothiazolyl-(2)-carbinol in Experiment 4. The ingredients and their quantities were: 3.36 g (0.015 mole) stannous chloride and 12.5 ml concentrated hydrochloric acid. 60 ml 20% aqueous sodium hydroxide solution was required to separate the synthesized aminocarbinol from the acid solution. The aminocarbinol yield was 2.4 g (82.4%). The product was purified by crystallization from ample xylol (charcoal was used) and was washed in petroleum ether. Methyl-[6-aminobenzothiazolyl-(2)-carbinol was obtained as transparent and virtually colorless needles, m.p. 220°. The aminocarbinol was readily soluble without heating in dilute (1 : 5) hydrochloric acid, and combined to form a diazo compound, which, with β-naphthol, gave an orange-red dye as product.

Found %: N 14.33, 14.34. $C_9H_{10}ON_2S$. Calculated %: N 14.43.

17. Methyl-[6-nitrobenzothiazolyl-(2)]-ketone. (XVII). This ketone was obtained by oxidizing methyl-[6-nitrobenzothiazolyl-(2)]-carbinol with chromium trioxide in an acetic acid medium in a manner similar to the synthesis of methyl-benzothiazolyl-(2)-ketone previously proposed by us [2].

2.6 g (0.026 mole) chromium trioxide in 10 ml glacial acetic acid and 3 ml water was added through a dropping funnel to a hot solution (110°) of 6.7 g (0.03 mole) methyl-[6-nitrobenzothiazolyl-(2)]-carbinol in 25 ml glacial acetic acid at such a rate as to cause the liquid to boil moderately at its surface. This addition took only a few minutes. The mixture was then boiled for 5 minutes and stirred for another 10 minutes without heating. When cooled, the mixture was diluted with 50 ml water, and the precipitate thus formed was filtered and washed in 20% aqueous acetic acid until the wash liquid became colorless. The ketone yield was 5.6 g (84% of the theoretical). The ketone was recrystallized in its entirety from a 100 ml mixture of dioxan (1 volume) and ethyl alcohol (2 volumes), the mother liquors being decolorized with ample charcoal. The product consisted of yellowish needles, m.p. 188°. For purposes of analysis, the ketone was recrystallized twice more, the first time from ethyl alcohol, and the second from the mixture described above, the product being pale-yellow needles, m.p. 191°.

Found %: N 12.74, 12.58. $C_9H_8O_3N_2S$. Calculated %: N 12.61.

Unlike methyl-benzothiazolyl-(2)-ketone, having a strong, pleasant aroma, the present ketone had no odor. The thiosemicarbazone ketone, prepared in the usual manner (with an 83% yield), consisted, after double crystallization from ample isobutyl alcohol, of small yellow crystals with a marked decomposition temperature of 272°.

18. Oxidation of methyl-[6-nitrobenzothiazolyl-(2)]-ketone. 0.75 g potassium permanganate dissolved in 20 ml water was poured into a hot suspension of 0.3 g methyl-[6-nitrobenzothiazolyl-(2)]-ketone in 40 ml water. The mixture was boiled for 10 minutes and the manganese dioxide precipitate was filtered off. 1 ml hydrochloric acid was added to the warm yellow filtrate, and the 6-nitrobenzothiazole-(2)-carboxylic acid thus precipitated was filtered off after half an hour, washed with water and air dried. 0.2 g nitro acid was obtained, and decarboxylated by careful heating in a test tube. The decarboxylation product was recrystallized from 8 ml ethyl alcohol (with charcoal), and 0.1 g of virtually colorless 6-nitrobenzothiazole crystals, melting at 175°, was obtained; when mixed with 6-nitrobenzothiazole of known composition (m.p. 174°), it melted at 174°.

SUMMARY

1. Nitration of benzothiazole-(2)-carbinol and methyl-[benzothiazolyl-(2)]-carbinol, dissolved in concentrated sulfuric acid, by nitric acid (d 1.52), produced satisfactory yields of the 6-nitro derivatives of these alcohols. Certain conversions of nitrobenzothiazolylcarbinols were studied, and some new 6-nitro- and 6-amino-substituted benzothiazole series compounds were obtained, as well as 2-chloromethyl and 2-(α-chloroethyl)-benzothiazoles.

2. An improved method of producing 6-nitrobenzothiazolyl-(2)-aldehyde, and convenient methods of synthesizing methyl-[6-nitrobenzothiazolyl-(2)]-ketone, benzothiazole-(2)- and 6-nitrobenzothiazole-(2)-carboxylic acids were proposed.

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SYNTHESIS OF NITRO, AMINO, AND HYDROXY DERIVATIVES IN THE DIPHENYLETHANE SERIES

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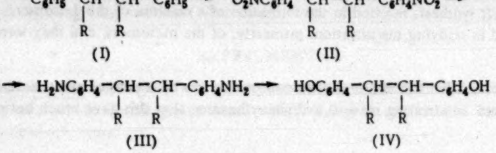
The p,p'-dihydroxy derivatives of diphenylethane (IV) are known [1] to include such most physiologically active compounds as meso-p,p'-dihydroxy-2,3-diphenylbutane (IV, R = CH_3), meso-p,p'-dihydroxy-3,4-diphenylhexane (IV, R = C_2H_5), meso-p,p'-dihydroxy-4,5-diphenyloctane (IV, R = C_3H_7) and others of marked estrogenic effect.

Moreover, compounds having high curare-like activity [2] have been found among the p,p'-diammonium derivatives of the diphenylethanes.

In this connection, a series of p,p'-diamino derivatives of diphenylethane were synthesized and converted, on the one hand, into p,p'-dihydroxy derivatives and, on the other, into p,p'-diammonium derivatives.

The present paper describes the synthesis of hydrocarbons of the diphenylethane series (I) and their conversion into p,p'-dinitro (II), p,p'-diamino (III) and p,p'-dihydroxy derivatives (IV).

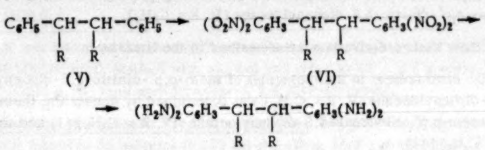


$$\underset{\text{(I)}}{C_6H_5-\underset{R}{CH}-\underset{R}{CH}-C_6H_5} \rightarrow \underset{\text{(II)}}{O_2NC_6H_4-\underset{R}{CH}-\underset{R}{CH}-C_6H_4NO_2} \rightarrow$$

$$\rightarrow \underset{\text{(III)}}{H_2NC_6H_4-\underset{R}{CH}-\underset{R}{CH}-C_6H_4NH_2} \rightarrow \underset{\text{(IV)}}{HOC_6H_4-\underset{R}{CH}-\underset{R}{CH}-C_6H_4OH}$$

($R = H, CH_3, C_2H_5, C_3H_7$ and C_4H_9).

Further, tetranitro (VI) and tetraamino derivatives (VII) were obtained from meso-3,4-diphenylhexane (V).

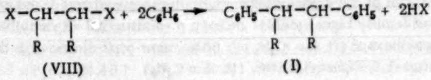


$$\underset{\text{(V)}}{C_6H_5-\underset{R}{CH}-\underset{R}{CH}-C_6H_5} \rightarrow \underset{\text{(VI)}}{(O_2N)_2C_6H_3-\underset{R}{CH}-\underset{R}{CH}-C_6H_3(NO_2)_2} \rightarrow$$

$$\rightarrow \underset{\text{(VII)}}{(H_2N)_2C_6H_3-\underset{R}{CH}-\underset{R}{CH}-C_6H_3(NH_2)_2}$$

($R = C_2H_5$).

The simplest system for obtaining these hydrocarbons is undoubtedly the following:



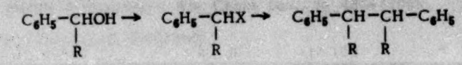
$$\underset{\text{(VIII)}}{X-\underset{R}{CH}-\underset{R}{CH}-X} + 2C_6H_6 \rightarrow \underset{\text{(I)}}{C_6H_5-\underset{R}{CH}-\underset{R}{CH}-C_6H_5} + 2HX$$

(R = hydrogen or alkyl; X = halide).

However, this method is convenient only when the required dihalide derivatives are available.

The synthesis of diphenylethane (I, R = H) by this method has been described [3,4] and was repeated by us. We also used this method, starting with 2,3-dibromobutane [5], to synthesize 2,3-diphenylbutane (I, R = CH_3) [6,7] although the yield of meso-forms of this compound was not large.

To obtain 3,4-diphenylhexane (I, R = C_2H_5) [8], 4,5-diphenyloctane (I, R = C_3H_7) [9] and 5,6-diphenyldecane (I, R = C_4H_9) [9,10], described in the literature, the following system was used:



$$C_6H_5{-}\underset{\displaystyle R}{\underset{|}{C}}HOH \rightarrow C_6H_5{-}\underset{\displaystyle R}{\underset{|}{C}}HX \rightarrow C_6H_5{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}C_6H_5$$

(IX) (X) (I)

($R = C_2H_5$, C_3H_7 or C_4H_9; X = chlorine).

The carbinols, specifically ethylphenylcarbinol (IX, $R = C_2H_5$) [8,10], propylphenylcarbinol (IX, $R = C_3H_7$) [11] and butylphenylcarbinol (IX, $R = C_4H_9$) [11] have been described. We produced them by the Grignard reaction from the corresponding alkyl haloid (ethyl bromide, propyl chloride or butyl bromide) and benzaldehyde.

Conversion of the carbinols into the homologous chlorides – 1-phenyl-1-chloropropane (X, $R = C_2H_5$), 1-phenyl-1-chlorobutane (X, $R = C_3H_7$) and 1-phenyl-1-chloropentane (X, $R = C_4H_9$), was performed by the method described in the literature [12] of reacting the carbinols with thionyl chloride. 1-Phenyl-1-chloropropane was also obtained by saturating phenylethylcarbinol with hydrogen chloride [13,14]. Phosphorous trichloride was used in this instance to cause completion of the reaction. The addition of this last compound to the saturation product took place after removal of the layer of water formed during the saturation process.

3,4-Diphenylhexane (I, $R = C_2H_5$), 4,5-diphenyloctane (I, $R = C_3H_7$) and 5,6-diphenyldecane (I, $R = C_4H_9$), are known to be able to be derived from the corresponding halo derivatives when the latter are reacted with sodium [8,9], magnesium [10] or iron [14], although the hydrocarbon yield is not high. We found that of these three metals, magnesium gives the best results in reaction with 1-phenyl-1-chloropropane (X, $R = C_2H_5$), and we also used it in reaction with 1-phenyl-1-chlorobutane (X, $R = C_3H_7$) and 1-phenyl-1-chloropentane (X, $R = C_4H_9$).

It must be noted that all the hydrocarbons we synthesized, except diphenylethane, contained two assymetrical carbon atoms, so that their synthesis resulted in the formation of a mixture of the d-isomer, l- isomer and the mesomer. We were interested in studying the nitration, primarily, of the mesomers, and they were therefore isolated from the mixtures by alcohol.

Nitration of the hydrocarbons to obtain dinitro compounds was by means of nitric acid in a medium of acetic anhydride, as we had found in nitrating meso-3,4-diphenylhexane that this gave much better yields than other methods of nitration.

Thus, the following p,p'-dinitro derivatives were synthesized: p,p'-dinitro-1,2-diphenylethane (II, R = H) [15,16], meso-p,p'-dinitro-2,3-diphenylbutane (II, $R = CH_3$) [17], meso-p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$) [18], racemic p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$) [18], meso-p,p'-dinitro-4,5-diphenyloctane (II, $R = C_3H_7$) and meso-p,p'-dinitro-5,6-diphenyldecane (II, $R = C_4H_9$).

The first four of these dinitro derivatives are described in the literature.

The position of the nitro radical in the molecules of meso-p,p'-dinitro-4,5-diphenyloctane (II, $R = C_3H_7$) and meso-p,p'-dinitro-5,6-diphenyldecane (II, $R = C_4H_9$) was determined by converting them into their known dihydroxy derivative homologs: meso-p,p'-dihydroxy-4,5-diphenyloctane (IV, $R = C_3H_7$) [1] and meso-p,p'-dihydroxy-5,6-diphenyldecane (IV, $R = C_4H_9$) [14].

Comparison of the yields of the dinitro derivatives obtained shows that the presence of two alkyls in the 1,2-positions greatly facilitates entry of the nitro radical into the p and p'-positions.

Thus, for example, the yield of p,p'-dinitro-1,2-diphenylethane (II, R = H) attained only 20% of the theoretical, while, when the meso-forms of the diphenylethane homologs were nitrated, the corresponding dinitro derivatives were obtained with considerably higher yields: meso-p,p'-dinitro-2,3-diphenylbutane (II, $R = CH_3$) 51%, meso-p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$) 66%, meso-p,p'-dinitro-4,5-diphenyloctane (II, $R = C_3H_7$) 62.1%, and meso-p,p'-dinitro-5,6-diphenyldecane (II, $R = C_4H_9$) 64.5%.

Nitration of meso-3,4-diphenylhexane (V) with the nitrating mixture gave meso-o,o',p,p'-tetranitro-3,4-diphenylhexane (VI).

This substance had been obtained by Fodor and Wein [18], but they took it erroneously for a trinitro derivative.

We confirmed the composition of this tetranitro derivative by elementary analysis. By reduction, we obtained the homologous tetraamino derivative (VII), whose composition was also confirmed by analysis. We obtained this same tetranitro derivative by reacting the nitrating mixture with meso-p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$). It is clear from the foregoing that this compound apparently is described by formula (VI).

We usually employed iron filings and a mixture of acetic and hydrochloric acids to reduce the dinitro derivatives. Thus we obtained p,p'-diamino-1,2-diphenylethane (III, R = H) [15], meso-p,p'-diamino-2,3-diphenylbutane (III, R = CH_3) [19], meso-p,p'-diamino-3-4-diphenylhexane (III, R = C_2H_5) [18,20], racemic p,p'-diamino-3,4-diphenylhexane (III, R = C_2H_5) [18,20], meso-p,p'-diamino-4,5-diphenyloctane (III, R = C_3H_7) and meso-p,p'-diamino-5,6-diphenyldecane (III, R = C_4H_9).

Isolation of racemic p,p'-diamino-3,4-diphenylhexane (III, R = C_2H_5) after reduction with iron filings proved difficult. We reduced racemic p,p'-dinitro-3,4-diphenylhexane with stannous chloride.

The literature contains two different melting points for racemic p,p'-diamino-3,4-diphenylhexane, i.e., 63-65° [20] and 80°[18]. We obtained this compound with an m.p. of 70-71°. This difference in melting point is apparently to be explained by an admixture of the meso-form in the racemate. We removed the meso-form contaminant from the racemate by use of the low solubility of the hydrochloride of this compound in hydrochloric acid.

The following p,p'-dihydroxy derivatives were obtained by diazotizing the p,p'-diamino-1,2-diphenylethane homologs in a hydrochloric acid solution, followed by decomposition of aqueous solutions of the diazo compounds by heat: meso-p,p'-dihydroxy-2,3-diphenylbutane (IV, R = CH_3) [1], meso-p,p'-dihydroxy-3,4-diphenylhexane (IV, R = C_2H_5) [1], meso-p,p'-dihydroxy-4,5-diphenyloctane (IV, R = C_3H_7) [1], and meso-p,p'-dihydroxy-5,6-diphenyldecane (IV, R = C_4H_9) [14]. These p,p'-dihydroxy derivatives have all been described previously, but only meso-p,p'-3,4-dihydroxy-diphenylhexane (IV, R = C_2H_5) had been obtained by diazotization of the diamino derivative homolog [18].

Our experiments showed that at the point at which the foregoing p,p'-dihydroxy derivatives are produced from the corresponding p,p'-diamino derivatives, the readiness with which the amino group is converted to the hydroxy group was dependent to a considerable degree upon the length of the carbon chains in the 1,2-positions; the best results were obtained with methyl and ethyl radicals (60 to 73%).

EXPERIMENTAL

Meso-2,3-diphenylbutane. 53.7 g (30 ml) 2,3-dibromobutane was added in 40 minutes, with stirring and cooling of the mixture by salt and ice, to 7.8 g aluminum trichloride and 88 ml distilled benzene, stirring being continued for another 4.5 hours.

The next day the contents of the reaction flask were poured into 200 ml water, carefully shaken, the aqueous layer extracted with 30 ml benzene, the benzene solution washed in 20 ml water and distilled. Upon distillation of the benzene and redistillation the following fractions were obtained: 1st to 145° / 26 mm, 6.7 g; 2nd 150-195° 27 mm, 16.7 g; residue 10.4 g.

42 ml ethyl alcohol was added to the second fraction, and the whole was heated until dissolved. On the following day the precipitate was filtered, washed with alcohol and dried at 50°. 4.8 g meso-2,3-diphenylbutane, m.p. 123-125° was obtained. Yield 9.1%, measured in terms of 2,3-dibromobutane.

Meso-3,4-diphenylhexane and racemic 3,4-diphenylhexane. 174 g 1-phenyl-1-chloropropane (b.p. 95-99° / 22 mm) in 75 ml ether was added in 50 minutes to 120 ml dry ether, 15.2 g magnesium filings, and 0.75 g iodine that had been heated together until the ether began to boil. The reaction usually began in 5 to 10 minutes after the first 10 ml of the chloride solution had been added, as could be seen from the appearance of a gray precipitate, and it continued with evolution of heat. The reaction was accompanied by vigorous boiling of the ether, which was controlled by the rate at which the chloride was added and by the amount of heating; heating was continued for 7 hours after the last of the chloride had been added. Then, under water cooling, the following were gradually added to the reaction mixture: 75 ml water followed by a solution of 75 ml concentrated hydrochloric acid and 75 ml water. The supernatant ether layer was washed with water, the ether and the low boiling fraction were distilled over a boiling water bath, toward the end in a 17 mm vacuum. 175 ml ethyl alcohol was added to the residue, which was then heated until dissolved, and the mixture was cooled with salt and ice overnight.

The precipitate was filtered, washed with alcohol and dried at 40-50°. 12.5 g meso-3,4-diphenylhexane, m.p. 86.87°, was obtained.

The alcoholic mother liquor was distilled. 130 ml alcohol was added to the fraction collected between 162° / 19 mm and 192° / 15 mm, totalling 65 g, whereupon another 8.5 g meso-3,4-diphenylhexane, m.p. 88-89° was obtained in exactly the same manner as before. The total yield of meso-3,4-diphenylhexane was 21 g, constituting 15.5%, measured in terms of the chloride.

The alcoholic mother liquor was distilled at normal pressure with the purpose of isolating racemic 3,4-diphenylhexane. A 42 g fraction obtained between 286 and 300° was redistilled. 35 g racemic 3,4-diphenylhexane, b.p. 292-302°, was obtained in this manner. The yield of racemic 3,4-diphenylhexane was 26.1% in terms of chloride.

11.3 g magnesium filings, 70 ml dry ether and 0.5 g iodine were used to produce 3,4-diphenylhexane from an ether solution of the undistilled 1-phenyl-1-chloropropane obtained by saturation of 110 g ethylphenylcarbinol with hydrogen chloride. There was an 18% yield of 3,4-diphenylhexane, and a 26% yield of the racemic form, in terms of ethylphenylcarbinol.

Meso-4,5-diphenyloctane. This compound was obtained under the same conditions as meso-3,4-diphenylhexane. By reacting 8.5 g magnesium filings in the presence of 0.4 g iodine and 70 ml dry ether with 107 g 1-phenyl-1-chlorobutane (b.p. 115-118° / 15-18 mm) dissolved in 30 ml ether, a fraction consisting of 33 g, b.p. 172-200° / 16 mm was obtained after the usual processing and distillation (no portion of the meso-4,5-diphenyloctane was isolated prior to distillation). 11.3 g precipitate was obtained from the above fraction after addition of 33 ml ethyl alcohol. 6.9 g meso-4,5-diphenyloctane, m.p. 97-98° was obtained after recrystallization from 40 ml alcohol. The yield was 8.2% calculated in terms of 1-phenyl-1-chlorobutane.

Meso-5,6-diphenyldecane. This was obtained in the same manner as meso-4,5-diphenyloctane. By reacting 4.5 g magnesium filings in presence of 0.2 g iodine and 35 ml dry ether with 62 g 1-phenyl-1-chloropentane (b.p. 115-120° / 15-16 mm) dissolved in 10 ml ether, a 21 g fraction, b.p. 196-220° / 16 mm was obtained after the usual processing and distillation. 9.6 g precipitate was obtained from this fraction by means of 21 ml ethyl alcohol. After recrystallization from 40 ml alcohol, 5.6 g meso-5,6-diphenyldecane, m.p. 78-79° was obtained. The yield was 12.4%, measured in terms of 1-phenyl-1-chloropentane.

p,p'-Dinitro-1,2-diphenylethane. 14 ml nitric acid (d 1.39) was added in 1 hour 15 minutes, with stirring and cooling by water for a reaction mixture temperature of 15-25°, to 10 g 1,2-diphenylethane (m.p. 50-52°) and 120 ml acetic anhydride. Stirring continued another 4.5 hours.

The next day, 50 ml water was added in an hour, with stirring and cooling; the precipitate was isolated by filtering, washed in dilute acetic acid and dried at 80°. Weight 9.7 g. The precipitate was then boiled with 50 ml ethyl alcohol, filtered while hot, and the undissolved portion washed on the filter with hot alcohol. Weight 3.8 g. M.p. 171-176°. After cooling of the alcoholic mother liquor, 3 g precipitate, m.p. 60-70° was obtained, but it failed to yield p,p'-dinitro-1,2-diphenylethane even after repeated recrystallization.

After recrystallization of the 3.8 g precipitate (171-176°) from 115 ml benzene, 3 g p,p'-dinitro-1,2-diphenylethane was obtained, m.p. 179-181°. Yield was 20% in terms of 1,2-diphenylethane.

The p,p'-dinitro derivatives described below were obtained in the same manner.

Meso-p,p'-dinitro-2,3-diphenylbutane. To 7 g meso-2,3-diphenylbutane (m.p. 123-125°) and 77 ml acetic anhydride was added, as in the previous experiment, 10 ml nitric acid (d 1.39). 7 ml water was added to the reaction mixture on the following day. The precipitate obtained was filtered and dried at 120°. The weight of the precipitate was 6.6g. After recrystallizing the precipitate from 250 ml acetic acid there was obtained 5.1 g meso-p,p'-dinitro--2,3-diphenylbutane, m.p. 254-256°, white in color. Yield was 51%.

Found %: N 9.27, 9.34. $C_{16}H_{16}O_4N_2$. Calculated %: N 9.33.

Meso-p,p'-dinitro-3,4-diphenylhexane. 33 g meso-3,4-diphenylhexane (m.p. 86-87°) was nitrated in 330 ml acetic anhydride by 41 ml nitric acid (d 1.39). The next day 54 ml water was added, the precipitate was filtered, washed with acetic acid and dried at 100°. The precipitate weighed 34.1 g, m.p. 170-172°; yield 75%. After recrystallization from 285 ml acetic acid, 30 g meso-p,p'-dinitro-3,4-diphenylhexane was obtained, m.p. 171-173°, color white. Yield 66%.

Found %: C 65.74, 65.63; H 6.21, 6.10; N 8.42, 8.84. $C_{18}H_{20}O_4N_2$. Calculated %: C 65.85; H 6.10; N 8.54.

Meso-p,p'-dinitro-4,5-diphenyloctane. After nitration of 5.6 g meso-4,5-diphenyloctane (m.p. 97-98°) in 50 ml acetic anhydride by 6.2 ml nitric acid (d 1.39), and addition of 8.1 ml water to the reaction mixture, after 12 hours the precipitate was filtered, and it weighed, after washing in dilute acetic acid and drying at 80°, 5.6 g, m.p. 161-165°.

After recrystallization from 40 ml acetic acid, 4.65 g meso-p,p'-dinitro-4,5-diphenyloctane, white in color, m.p. 170-171.5°, was obtained. Yield 62.1%.

0.1514, 0.1400 g sub.: 0.3742, 0.3466 g CO_2; 0.0920, 0.0857 g H_2O. 0.3052, 0.2269 g sub.: 20.8 ml N_2 (19°, 734 mm); 15.5 ml N_2 (20°, 740 mm). Found %: C 67.41, 67.51; H 6.80, 6.85; N 7.70, 7.75. $C_{20}H_{24}O_4N_2$. Calculated %: C 67.42; H 6.74; N 7.87.

Meso-p,p'-dinitro-5,6-diphenyldecane. 8 g meso-5,6-diphenyldecane (m.p. 78-79°) was nitrated in 66 ml acetic anhydride by 8.2 ml nitric acid (d 1.39). The next day, 10.8 ml water was added, the precipitate filtered, washed with acetic acid and dried at 80°. The weight was 8.2 g, the m.p. 147-149°. After recrystallization from 50 ml acetic acid, 6.75 g meso-p,p'-dinitro-5,6-diphenyldecane was obtained, white in color and with an m.p. of 153-155°. Yield was 64.6%.

0.0961, 0.1964 g sub.: 0.2406, 0.4948 g CO_2; 0.0646, 0.1266 g H_2O. 0.3096, 0.2876 g sub.: 19.20 ml N_2 (20°, 762 mm); 18.3 ml N_2 (29°, 739.4 mm). Found %: C 68.32, 68.75; H 7.52, 7.21; N 7.20, 7.00. $C_{22}H_{28}O_4N_2$. Calculated %: C 68.75; H 7.29; N 7.29.

Racemic p,p'-dinitro-3,4-diphenylhexane. 40 g racemic 3,4-diphenylhexane (b.p. 292-302°) was nitrated in 400 ml acetic anhydride by 50 ml nitric acid (d 1.39). Next day, 650 ml water was added. The nitration product separated out as a viscous mass. After repeated washing by decanting with water, separation of the water layer and drying at 100°, 55.4 g impure racemic p,p'-dinitro-3,4-diphenylhexane (an oil), was obtained, out of which a small quantity of meso-p,p'-dinitro-3,4-diphenylhexane crystals precipitated after 15 days.

Meso-o,o',p,p'-tetranitro-3,4-diphenylhexane. 10 g meso-3,4-diphenylhexane (m.p. 86-87°) was added in 10 minutes, with stirring and cooling, to a nitrating mixture composed of 80 ml sulfuric acid (d 1.84) and 40 ml nitric acid (d 1.51). The whole was then stirred and heated for two hours over a water bath at a temperature of 46-48° in the reaction mixture; after cooling it was poured into a mixture of water and ice. The precipitate was filtered and dried at 60°. The weight was 17.2g. Recrystallization from 480 ml acetic acid gave 11.6 g meso-o,o',p,p'-tetranitro-3,4-diphenylhexane, m.p. 216-218° (corrected), white in color, with a pale yellow tint. Yield was 66%.

0.1505, 0.1724 g sub.: 0.2859, 0.3286 g CO_2; 0.0619, 0.0706 g H_2O. 0.1974, 0.1540 g sub.: 24.3 ml N_2 (21°, 731 mm); 18.5 ml N_2 (22°, 733 mm). Found %: C 51.80, 51.98; H 4.60, 4.58; N 13.75, 13.41. $C_{18}H_{18}O_8N_4$. Calculated %: C 51.67; H 4.31; N 13.40.

p,p'-Diamino-1,2-diphenylethane. 5.8 g p,p'-dinitro-1,2-diphenylethane (m.p. 179-181°) was dissolved with heating in 105 ml acetic acid, whereupon 17.4 g iron shavings and 105 ml hydrochloric acid (d 1.19) were added together, the first, however, within 30 minutes, and the second in 2.5 to 3 hours. The reaction was conducted with an air condenser, under constant heating to 100-110° of the reaction mixture. After dissolution of the iron filings the mixture of acetic and hydrochloric acids was distilled over a boiling water bath at a final pressure of 50-60 mm. 417 ml saturated sodium chloride solution was added to the dry residue, and the mixture was heated for half an hour over a boiling water bath to dissolve the iron chloride.

The next day, the residue of impure dihydrochloride of the diamino product was filtered off, washed repeatedly with a saturated sodium chloride solution, dissolved with heating in 400 ml water, the solution boiled 20 minutes with 1.5 g activated charcoal, filtered, and the hot filtrate poured into 15 ml concentrated ammonia solution, diluted with 40 ml water. After cooling the residue of impure diamino product was filtered off and recrystallized from 3500 ml water in the presence of 1 g activated charcoal. This gave 3.1 g p,p'-diamino-1,2-diphenylethane having a very faint violet tint, m.p. 137-139°. Yield was 68.6%. The meso-diamino derivatives described below were obtained in the same manner and purified out of dilute alcohol.

Meso-p,p'-diamino-2,3-diphenylbutane. 11.2 g meso-p,p'-dinitro-2,3-diphenylbutane (m.p. 254-256°) was dissolved with heating in 535 ml acetic acid and reduced by the addition of 30.3 g iron filings and 198 ml hydrochloric acid (d 1.19). The reaction mixture was heated for 8 hours until complete solution of the iron. After processing conducted as in the preceding experiment, an impure diamino product precipitate separated out, which was boiled in the presence of activated charcoal in 120 ml ethyl alcohol diluted with 20 ml water. The hot filtrate was dissolved in 200 ml hot water. Upon drying at 100°, this gave 6 g meso-p,p'-diamino-2,3-diphenylbutane, white in color, m.p. 170-172°. Yield was 67%.

Found %: N 11.50, 11.46; $C_{16}H_{20}N_2$. Calculated %: N 11.67.

Meso-p,p'-diamino-3,4-diphenylhexane. Reduction of 15 g meso-p,p'-dinitro-3,4-diphenylhexane (m.p. 171-172°) in 225 ml acetic acid solution was performed by addition of 36.7 g iron filings and 225 ml hydrochloric acid (d 1.19).

The impure diamino precipitate produced after processing was boiled in the presence of activated charcoal in

150 ml ethyl alcohol, dissolved in 30 ml water. The hot filtrate was dissolved in 300 ml water. After drying at 80°, this gave 10.1 g precipitated meso-p,p'-diamino-3,4-diphenylhexane, white in color, m.p. 140-142°. Yield 82.4%.

Found %: C 80.21, 80.12; H 8.71, 8.60. $C_{18}H_{24}N_2$. Calculated %: C 80.60; H 9.00.

Meso-p,p'-diamino-4-5,diphenyloctane. 3 g meso-p,p'-dinitro-4,5-diphenyloctane (m.p. 170-171.5°) dissolved in 42 ml acetic acid was reduced by the addition of 6.9 g iron filings and 42 ml hydrochloric acid (d 1.19). After distillation of the acid mixture and treatment of the dry residue with 190 ml saturated sodium chloride solution, the diamino dihydrochloride product precipitate separated out, and was then dissolved upon heating in 350 ml water. The solution was boiled with activated charcoal, filtered, and the hot filtrate poured into a dilute ammonia solution.

The impure diamino precipitate was boiled in the presence of activated charcoal in 30 ml ethyl alcohol, and the hot filtrate was diluted with 35 ml hot water. After drying at 80°, 2 g white precipitated meso-p,p'-diamino-4,5-diphenyloctane, m.p. 129-130°, was obtained. Yield 80%.

0.0888, 0.1924 g sub.: 0.2643, 0.5724 g CO_2; 0.0762, 0.1668 g H_2O. 0.1976, 0.2039 g sub.: 16.7 ml N_2 (23°, 742 mm); 16.45 ml N_2 (21.5°, 740 mm). Found %: C 81.22, 81.18; H 9.60, 9.70; N 9.51, 9.14. $C_{20}H_{28}N_2$. Calculated %: C 81.08; H 9.46; N 9.46.

Meso-p,p'-diamino-5,6-diphenyldecane. 4.3 g meso-p,p'-dinitro-5,6-diphenyldecane (m.p. 153-155°) dissolved in 56 ml acetic acid was reacted with 9.2 g iron filings and 56 ml hydrochloric acid (d 1.19), whereupon the usual processing produced an impure diamino product precipitate which was boiled in 30 ml ethyl alcohol diluted with 5 ml water, in the presence of activated charcoal. The hot filtrate was dissolved in 60 ml hot water. The diamino product, separated out in the form of oily drops, crystallized as it cooled. 2.87 g white meso-p,p'-diamino-5,6-diphenyldecane, m.p. 105-106.5° was obtained. Yield was 79.1%.

0.1720, 0.1141 g sub.: 0.5136, 0.3404 g CO_2; 0.1557, 0.1016 g H_2O. 0.2896, 0.2217 g sub.: 23.2 ml N_2 (24°, 732.2 mm); 18 ml N_2 (25.5°, 727.8 mm). Found %: C 81.49, 81.41; H 10.13, 9.96; N 8.87, 8.89. $C_{22}H_{32}N_2$. Calculated %: C 81.48; H 9.88; N 8.64.

Racemic p,p'-diamino-3,4-diphenylhexane. A solution of 36 g crystalline stannous chloride ($SnCl_2 \cdot 2H_2O$) in 38 ml hydrochloric acid (d 1.19), brought almost to he boiling point, was added in a few minutes to a solution, also almost boiling, of 7 g oily racemic p,p'-dinitro-3,4-diphenylhexane in 60 ml glacial acetic acid. The reaction mass was then heated for two hours at 80°.

On the following day most of the acetic and hydrochloric acid mixture was distilled off in vacuum over a water bath. 50 ml glacial acetic acid was added to the residue, and the precipitate deposited was filtered off after standing for 9 hours. The precipitate was dissolved in 150 ml water, and the tin was precipitated by hydrogen sulfide. The filtrate was evaporated till dry, and the dry residue dissolved in 15 ml hydrochloric acid (d1.19). If, at this point, the meso derivative hydrochloride was precipitated, it was filtered off. The filtrate was diluted with 50 ml water, boiled with activated charcoal and, when cooled, poured into a dilute ammonia solution. The precipitate was filtered out on the following day. The weight of the air-dried precipitate was 1.5 g. M.p. 65-67°. The rose-tinted precipitate was dissolved in 30 ml ether, the solution boiled with activated charcoal, filtered free of the charcoal after cooling, and hydrogen chloride was passed through the filtrate; this resulted in separation of an oily hydrochloride. The ether was poured off, and the hydrochloride was dissolved in 30 ml water, shaken cold with activated charcoal, and the filtrate poured into a dilute ammonia solution. This resulted in clouding at first, followed by precipitation after 10 to 12 hours. 1.16 g white racemic p,p'-diamino-3,4-diphenylhexane, m.p. 70-71° was obtained. Yield 20.3%.

0.1610, 0.1227 g sub.: 0.4759, 0.3622 g CO_2; 0.1296, 0.1000 g H_2O. 0.1616, 0.1505 g sub.: 14.1 ml N_2 (20°, 764.6 mm); 13.65 ml N_2 (21°, 740 mm). Found %: C 80.62, 80.50; H 9.01, 9.12; N 10.20, 10.25. $C_{18}H_{24}N_2$. Calculated %: C 80.60; H 9.00; N 10.44.

Meso-o,o',p,p'-tetraamino-3,4-diphenylhexane. 70 g stannous chloride dissolved in 172 ml hydrochloric acid (d 1.19) and brought almost to the boiling point was poured, in several doses during a few minutes time, into 8.6 g meso-o,o',p,p'-tetranitro-3,4-diphenylhexane (m.p. 216-218° – corrected) dissolved in 400 ml glacial acetic acid, also almost boiling, in a 2000 ml flask. The solution was then heated with an air condenser for an hour at almost the boiling pontt. On the following day the precipitate was filtered out, washed in acetic acid, and dried at 50°. White in color, and weighing 18.5 g, the precipitate was dissolved in 250 ml water, the tin precipitated by hydrogen sulfide, the filtrate evaporated to dryness, the residue dissolved in 150 ml water, the solution shaken for 30 minutes with 0.4 g activated charcoal, filtered, and the filtrate poured into a cooled solution of 8 ml concentrated ammonia in 50 ml water. This gave 4.28 g air-dried precipitate, white in color, m.p. 241-243°. The precipitate was dissolved in a mixture of 42 ml ethyl alcohol, 42 ml water, 12 ml hydrochloric acid (d 1.19), shaken at room temperature with activated charcoal and, the next day, after filtering, was poured, with cooling, into a solution of 85 ml alcohol and 27 ml concentrated ammonia. A crystalline deposit gradually began to precipitate. 3.7 g white meso-o,o'p,p'-tetraamino-3,4-diphenylhexane, m.p. 248-250° was obtained. Yield 60.3%.

0.1555, 0.1267 g sub.: 0.4130, 0.3360 g CO_2; 0.1202, 0.1000 g H_2O. 0.1262, 0.1148 g sub.: 20.8 ml N_2 (21°, 742.6 mm); 18.85 ml N_2 (24°, 763.5 mm). Found %: C 72.43, 72.32; H 8.65, 8.83; N 18.70, 18.95. $C_{18}H_{26}N_4$. Calculated %: C 72.48; H 8.72; N 18.79.

Meso-p,p'-dihydroxy-2,3-diphenylbutane. 2 g meso-p,p'-diamino-2,3-diphenylbutane (m.p. 170-172°) was dissolved in dilute hydrochloric acid (1400 ml water and 22 ml hydrochloric acid, d 1.15). and was diazotized with stirring at room temperature by a solution of 1.3 g sodium nitrite in 50 ml water. The whole was then stirred for an hour, the reaction flask placed in a water bath, heated to 75°, and the heating continued for another hour at a temperature of 90° in the flask. The precipitate was filtered off on the following day, then stirred at room temperature for several hours in a solution of 2 g potassium hydroxide in 135 ml water, the solution filtered free of a deposit that formed in negligible quantity, and the filtrate poured into dilute hydrochloric acid. The precipitate deposited was recrystallized in the presence of activated charcoal from 25 ml acetic acid diluted with 20 ml H_2O. 1.4 g white meso-p,p' dihydroxy-2,3-diphenylbutane, m.p. 229-231°, was obtained. Yield 69.4%. The dihydroxy derivatives described below were obtained in the same manner.

Found %: C 78.97; H 7.10. $C_{16}H_{18}O_2$. Calculated %: C 79.34; H 7.44.

Meso-p,p'-dihydroxy-3,4-diphenylhexane. Diazotization of 5 g meso-p,p'-diamino-3,4-diphenylhexane (m.p. 140-142°), dissolved in 3500 ml water and 55 ml hydrochloric acid (d 1.15) was performed by means of 3,3 g sodium nitrite solution in 125 ml water.

Dissociation of the diazo solution and purification of the deposited precipitate by means of a dilute potassium hydroxide solution proceeded as in the prior experiment. The alkali filtrate was poured into dilute hydrochloric acid, and the precipitate thus formed was dissolved in 125 ml ethyl alcohol diluted with 100 ml water, boiled with 2 g activated charcoal, filtered, and the hot filtrate dissolved in 125 ml hot water. 3.7 g white meso-p,p'-dihydroxy-3,4-diphenylhexane was obtained, m.p. 184-186°. Yield 73.4%.

A sample mixed with sinestrol obtained from anethol did not cause depression in m.p.

Found %: C 79.73; H 8.22. $C_{18}H_{22}O_2$. Calculated %: C 80.00; H 8.15.

Meso-p,p'-dihydroxy-4,5-diphenyloctane. 0.9 g meso-p,p'-diamino-4,5-diphenyloctane (m.p. 129-131°) was dissolved in 580 ml water and 4.6 ml hydrochloric acid, and diazotized by a solution of 0.5 g sodium nitrite in 25 ml water. The usual processing gave 0.4 g of a brownish impurity that did not dissolve in dilute potassium hydroxide solution. After neutralization, a precipitate was deposited by the alkaline filtrate. The weight of the precipitate, after drying at 80°, was 0.35 g, m.p. 164-165°. Yield 39%. After solution in 6 ml ethyl alcohol and dilution of the heated alcohol solution with 14 ml hot water 0.3 g white meso-p,p'-dihydroxy-4,5-diphenyloctane, m.p. 165-166° was obtained. Yield 33.1%.

Found %: C 80.38; H 9.04. $C_{20}H_{26}O_2$. Calculated %: C 80.54; H 8.72.

Meso-p,p'-dihydroxy-5,6-diphenyldecane. Diazotization of 1.2 g meso-p,p'-diamino-5,6-diphenyldecane (m.p. 105-106.5°), dissolved in 700 ml water and 5.5 ml hydrochloric acid, was performed by means of 0.6 g sodium nitrite solution in 25 ml water. The usual processing gave 0.8 g of a brown-colored admixture that would not dissolve in a dilute potassium hydrochloride solution. After neutralization, the alkali filtrate gave 0.17 g precipitate of yellow tint, m.p. 168-169°. Yield 14.1%. After dissolving this precipitate in 10 ml ethyl alcohol and dilution of the heated filtrate in 10 ml hot water, 0.06 g meso-p,p'-dihydroxy-5,6-diphenyldecane was obtained, m.p. 170-170.5°. Yield 5%. Substitution of hydrochloric acid for diazotization by an equivalent quantity of sulfuric acid failed to improve yield.

Found %: C 80.62; H 9.24. $C_{22}H_{30}O_2$. Calculated %: C 80.98; H 9.20.

SUMMARY

1. A series of 1,2-diphenylethane, meso-2,3-diphenylbutane, meso and racemic 3,4-diphenylhexane, meso-4,5-diphenyloctane and meso-5,6-diphenyldecane derivatives, containing nitro, amino and hydroxy groups at the p and p' positions, were obtained by a common procedure.

The properties of five compounds produced for the first time are described.

2. It was found that the presence of two alkyls in the 1-and 2-positions of diphenylethane facilitated entry of the nitro group into p and p′ positions.

3. Substitution of the amino group by the hydroxy group through diazotization and subsequent decomposition, revealed that this substitution, always conducted under identical conditions, gave satisfactory yields (60-70%) when methyls or ethyls are in the 1 and 2 positions in the p,p′-diaminodiphenylethane molecule. When alkyls have an extended carbon chain, the yield is reduced: n-propyls 33-39%, n-butyls 5-14%.

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* See Consultants Bureau English translation, page 475.

SYNTHESES BASED ON ANABASINE

VIII. SULFONATION OF ANABASINE WITH SULFURIC ACID

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In the preceding paper [1], sulfonation of anabasine with pyridine sulfotrioxide was described. In the present work results of a study of the sulfonation of anabasine (I) with sulfuric acid are given.

It has been possible to carry out the reaction under the conditions for the sulfonation of pyridine [2] , by heating a mixture of anabasine with a large excess of concentrated sulfuric acid, d 1.84 (4 moles of sulfuric acid per mole of anabasine) for a period of 15-18 hours at 280-300°. The sulfonic acid formed was isolated in the form of its barium salt. From it the sodium and potassium salts were obtained by exchange reactions. The sulfonic acid was obtained in free state by reacting an equimolecular amount of sulfuric acid with the barium salt. It was a crystalline compound which, upon heating to 350°, did not melt and did not decompose. Determination of the equivalent, and analysis of the barium, potassium, and sodium salts indicated that its molecular formula $C_{10}H_7N_2SO_3H$, corresponded to α,β-dipyridyl sulfonic acid.

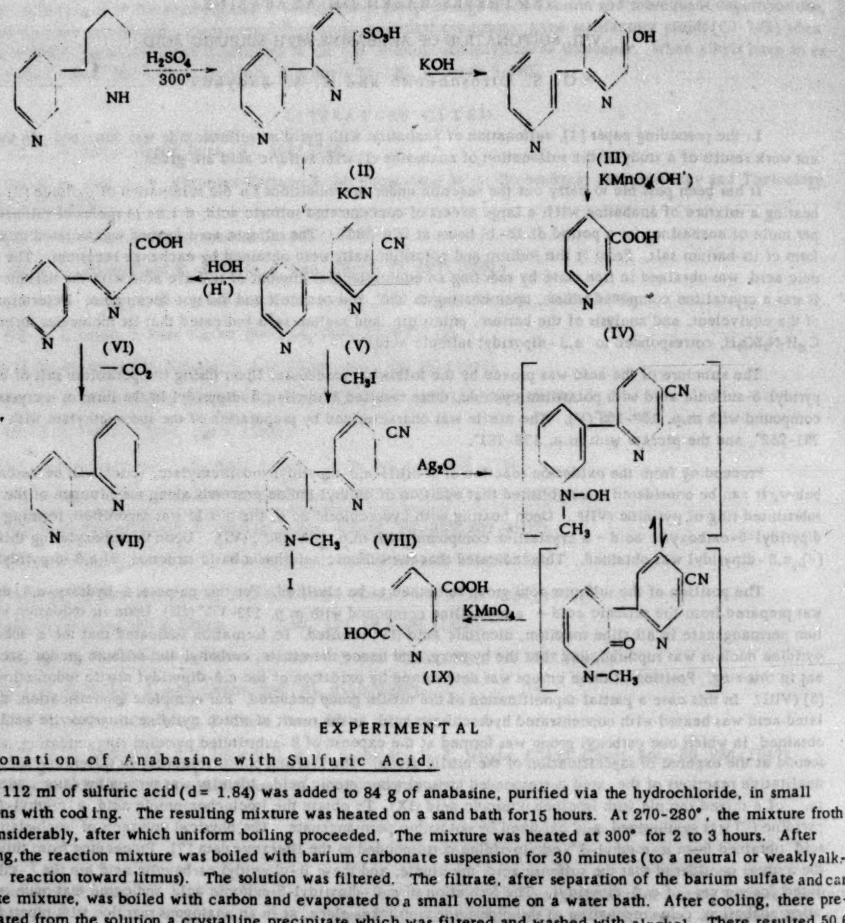
The structure of the acid was proved by the following procedure. Upon fusing the potassium salt of α,β-dipyridyl-5-sulfonic acid with potassium cyanide, there resulted 5-nitril-α,β-dipyridyl in the form of a crystalline compound with m.p. 108-109° (V). The nitrile was characterized by preparation of the iodomethylate with m.p. 251-252°, and the picrate with m.p. 179-181°.

Proceeding from the oxidation reaction of 5-nitril-α,β-dipyridyl iodomethylate, which will be described below, it can be considered as established that addition of methyl iodide proceeds along the nitrogen of the β-substituted ring of pyridine (VIII). Upon heating with hydrochloric acid, the nitrile was saponified, forming α,β-dipyridyl-5-carboxylic acid – a crystalline compound with m.p. 281-283°, (VI). Upon decarboxylating this acid, [4], α,β-dipyridyl was obtained. This indicated that the sulfonic acid has a basic structure of α,β-dipyridyl (VII).

The position of the sulfonic acid group remained to be clarified. For this purpose, 5-hydroxy-α,β-dipyridyl was prepared from the sulfonic acid – a crystalline compound with m.p. 178-179° (III). Upon its oxidation with potassium permanganate in alkaline medium, nicotinic acid (IV) resulted. Its formation indicated that the α-substituted pyridine nucleus was ruptured, and that the hydroxy, and hence the nitrile, carboxyl and sulfonic groups are present in this ring. Position of these groups was determined by oxidation of the α,β-dipyridyl nitrile iodomethylate [5] (VIII). In this case a partial saponification of the nitrile group occurred. For complete saponification, the isolated acid was heated with concentrated hydrochloric acid, as the result of which pyridine dicarboxylic acid was obtained, in which one carboxyl group was formed at the expense of β-substituted pyridine ring oxidation, and the second at the expense of saponification of the nitrile group. The melting point, solubility in water, and some other qualitative reactions of the acid corresponded to isocinchomeronic acid. Identity was proved by determining the m.p. of a mixed sample with isocinchomeronic acid (IX). To obtain the isocinchomeronic acid, α-methyl-β' ethyl pyridine [[illegible]] was synthesized, and oxidized by potassium permanganate. The physical constants of isocinchomeronic acid obtained from α-methyl-β'-ethylpyridine corresponded to the literature data [7]. Proceeding from this fact, the authors considered that the sulfonic acid, the nitrile, and the α,β-dipyridyl carboxylic acid are the β-substituted derivatives of α,β-dipyridyl. The formation of α,β-dipyridyl-5-sulfonic acid indicated that upon sulfonating anabasine, dehydrogenation of the piperidine ring takes place, as in an analogous reaction with piperidine[3].

To confirm the structure of 5-hydroxy-α,β-dipyridyl, it was necessary to carry out an additional study, since cases are known in the literature where the hydroxy group enters another position upon alkaline fusion of the sulfonic acid.

The scheme for sulfonation of anabasine and chemical conversion of the 5-sulfonic acid of α,β-dipyridyl is as follows.



EXPERIMENTAL

Sulfonation of Anabasine with Sulfuric Acid.

112 ml of sulfuric acid (d = 1.84) was added to 84 g of anabasine, purified via the hydrochloride, in small portions with cooling. The resulting mixture was heated on a sand bath for 15 hours. At 270-280°, the mixture frothed considerably, after which uniform boiling proceeded. The mixture was heated at 300° for 2 to 3 hours. After cooling, the reaction mixture was boiled with barium carbonate suspension for 30 minutes (to a neutral or weakly alkaline reaction toward litmus). The solution was filtered. The filtrate, after separation of the barium sulfate and carbonate mixture, was boiled with carbon and evaporated to a small volume on a water bath. After cooling, there precipitated from the solution a crystalline precipitate which was filtered and washed with alcohol. There resulted 50.6 g of the barium salt of 5-sulfonic acid of α,β-dipyridyl (yield 31.4 %). The mother liquor was evaporated and distilled at 174-178° (5-6 mm); an oil resulted in this case (picrate of the oil had a m.p. of 154-156°). A sample mixed with α,β-dipyridyl picrate had a m.p. of 160-162°.

The barium salt, recrystallized from water with added carbon, was in the form of a white cyrstalline product, with mother-of-pearl shade, insoluble in alcohol. The salt was dried in vacuo (1-2 mm) at 100°.

0.06348 g sub.: 0.02509 g $BaSO_4$. 0.12288 g sub.: 0.04779 g $BaSO_4$. Found %: Ba 22.33, 22.89. $C_{10}H_7N_2SO_3 \cdot \frac{1}{2}Ba$. Calculated %: Ba 22.65.

α,β-Dipyridyl-5-sulfonic acid Potassium Salt. Prepared by adding an equimolecular amount of potassium carbonate to a solution of the barium salt; the filtrate, after separation of the barium carbonate, was evaporated. Alcohol was added to the solution. A precipitate crystallized upon standing, which was then recrystallized from water with added alcohol. The potassium salt was soluble in water, insoluble in alcohol.

0.10845 g sub.: 0.03439 g K_2SO_4. 0.10828 g sub.: 0.03499 g K_2SO_4. Found %: K 14.17, 14.44. $C_{10}H_7N_2SO_3K$. Calculated %: K 14.18.

Sodium Salt of α,β-Dipyridyl-5-sulfonic Acid. Prepared in a manner analogous to that for the potassium salt. After separation of the $BaCO_3$ precipitate, the filtrate was evaporated to dryness. The salt was recrystallized from alcohol. The sodium salt was readily soluble in water, poorly so in alcohol, and when air-dried, contained 1 molecule of water of crystallization.

0.060441 g sub.: 0.014716 g Na_2SO_4. 0.071014 g sub.: 0.017623 g Na_2SO_4. Found %: Na 7.89, 7.05. $C_{10}H_7N_2SO_3Na \cdot H_2O$. Calculated %: Na 7.80.

Determination of the water of crystallization was carried out by drying in vacuo at 2 mm and 150°.

0.2572 g sub.: 0.0299 g H_2O. $C_{10}H_7N_2SO_3Na \cdot H_2O$. Calculated: : 0.0314 g H_2O.

α,β-Dipyridyl-5-sulfonic Acid

The calculated amount of sulfuric acid was added to a solution of 10 g of the barium salt of α,β-dipyridyl-5-sulfonic acid. After removal of $BaSO_4$, the precipitate was evaporated on a water bath to small volume. The α,β-dipyridyl-5-sulfonic acid crystallized out from the solution upon standing, in the form of mother-of-pearl platelets. The acid was poorly soluble in water, insoluble in alcohol; it was recrystallized from water. For analysis, the acid was dried in vacuo (1 mm) at 100°.

0.0694, 0.0792 g sub.: 3.50, 3.40 ml 0.09901 N NaOH. Found: Equiv. 234.0, 235.3. $C_{10}H_7N_2SO_3H$. Calculated: Equiv. 237.0.

3.778, 3.422 mg sub.: 0.388 ml N_2 (16°, 731 mm); 0.378 ml N_2 (25°, 722 mm). Found %: N 11.11, 11.50. $C_{10}H_7N_2SO_3H$. Calculated %: N 11.81.

α,β-Dipyridyl-5-nitrile. 10 g of α,β-dipyridyl-5-sulfonic acid in potassium salt form was mixed thoroughly with 32 g of potassium cyanide; the mixture placed in a retort, was heated to 351°, whereupon the oil distilled off, crystallizing rapidly in the tube of the retort. Yield was 2.1 g (32.5%). The α,β-dipyridyl-5-nitrile was soluble in methyl alcohol, poorly so in ethyl alcohol and water, soluble in toluene with heat as well as in petroleum ether and benzene. The m. p. was 107-109° (from methyl alcohol, petroleum ether and toluene).

2.090, 3.012 mg sub.: 0.460, 0.625 ml N_2 (25°, 724 mm). Found %: N 23.01, 22.63. $C_{10}H_7N_2CN$. Calc. %: N 23.20.

The picrate was obtained by decanting off alcoholic solutions of α,β-dipyridyl-5-nitrile with picric acid. M. p. 180-182° (from alcohol).

2.255, 2.450 mg sub.: 0.415, 0.240 ml N_2 (24°, 724.5 mm). Found %: N 19.32, 19.73. $C_{10}H_7N_2CN \cdot C_6H_2(NO_2)_3OH$. Calculated %: N 20.44.

The Iodomethylate. 2 g of methyl iodide was added to a solution of 1 g of α,β-dipyridyl-5-nitrile. The precipitate crystallized from solution on the second day. There resulted 1.1 g of α,β-dipyridyl-5-nitrile iodomethylate, M. p. 243-245° (from water or methyl alcohol).

0.0314 g sub.: 0.0980 ml 0.1 N $AgNO_3$ (potentiometric titration). Found %: I 39.50. $C_{10}H_7N_2CN \cdot CH_3I$. Calc. %: I 39.10.

α,β-Dipyridyl-5-carboxylic Acid. 3 g of α,β-dipyridyl-5-nitrile was heated with concentrated hydrochloric acid for 6 hours. The solution was then evaporated to dryness. The residue was α,β-dipyridyl-5-carboxylic acid. 2.8 g (28.11%) of the acid was obtained.

α,β-Dipyridyl-5-carboxylic acid was very poorly soluble in water. It sublimed. M. p. 281-283° (from alcohol).

2.836, 2.871 mg sub.: 0.353 ml N_2 (20°, 729 mm); 0.362 ml N_2 (22°, 729 mm). Found %: N 13.92, 13.99. $C_{10}H_7N_2COOH$. Calculated %: N 14.0.

20.02, 21.09 mg sub.: 1.02, 1.01 ml 0.099 N NaOH. Found: Equiv. 198, 210. $C_{10}H_7N_2COOH$. Calc.: Equiv. 200.

α,β-Dipyridyl. 0.1 g of α,β-dipyridyl-5-carboxylic acid and 0.2 g of copper bronze were heated with 2 ml of benzene in a sealed tube at 210-230° for 4 hours. After breaking the seal, the solution was filtered. The residue, after distilling off the benzene, gave with picric acid in alcoholic solution a picrate melting at 164-165°. A sample mixed with α,β-dipyridyl picrate, obtained by dehydrogenation of anabasine, melted at 164-169°.

5-Hydroxy-α,β-dipyridyl. 9 g of potassium hydroxide was heated on a sand bath in a porcelain cup with 3 ml of water. 3 g of α,β-dipyridyl-5-sulfonic acid in the sodium salt form was added at a temperature of 190-200°. The mixture was stirred continuously. With increased temperature the melt solidified, and then liquified upon heating to 300°. Heating was continued for another 30 minutes, the melt then dissolved in a small volume of water, neutralized with hydrochloric acid, and extracted with ether. The ether extractions were dried. The ether was distilled off. The solid precipitate had a m. p. of 177-179° (from methyl alcohol). 5-Hydroxy-α,β-dipyridyl was poorly soluble in water and alcohol. It was readily soluble in acetone.

2.742 mg sub.: 0.392 ml N_2 (22°, 732 mm). 2.407 mg sub.: 0.482 ml N_2 (23°, 728 mm). Found %: N 15.97, 16.14. $C_{10}H_7N_2OH$. Calculated %: N 16.28.

The picrate was prepared by decanting off the alcoholic solution of 5-hydroxy-α,β-dipyridyl with picric acid. M.p. was 217-219° (from water).

Nicotinic Acid.

An excess of saturated potassium permanganate solution was added to 3 g of 5-hydroxy-α,β-dipyridyl in 20 % sodium hydroxide solution. Manganese dioxide was removed from the solution by filtration. The filtrate was evaporated to small volume and neutralized with hydrochloric acid. The acid was isolated in the form of its copper salt by adding to a neutral solution of copper acetate. The copper salt was decomposed with hydrogen sulfide. The acid, m.p. 221-222°, was prepared successfully from the resulting precipitate (identified as nicotinic acid). Upon decarboxylation, pyridine resulted. The picrate of pyridine had a m.p. of 164-165°.

3,6-Pyridinedicarboxylic Acid.

2.2 g of the iodomethylate of 5-nitrile-α,β-dipyridyl was dissolved with heating in 20 ml of water, and freshly-precipitated silver oxide (from 2 g of silver nitrate) added to the solution. The silver iodide precipitate was filtered off rapidly, and to the filtrate potassium permanganate gradually added. On the following day, the excess potassium permanganate was removed by addition of alcohol. After removal of manganese dioxide, the filtrate was evaporated to small volume and neutralized with concentrated hydrochloric acid. 0.2 g of the acid resulted. For complete saponification of the nitrile group, the acid was boiled with concentrated hydrochloric acid for 4 hours; the solution was then evaporated to dryness and the residue recrystallized from hot water. The acid dried at 100° (1 mm) had a m.p. of 252-253°.

SUMMARY

1. The sulfonation reaction of anabasine with sulfuric acid at 280-300° has been studied. It has been established that there takes place dehydrogenation of the piperidine ring of anabasine, forming α,β-dipyridyl-5-sulfonic acid.

2. The sodium, potassium and barium salts of α,β-dipyridyl-5-sulfonic acid have been prepared.

3. Starting with α,β-dipyridyl-5-sulfonic acid, there have been prepared: α,β-dipyridyl-5-nitrile, characterized as the picrate and the iodomethylate, and α,β-dipyridyl-5-carboxylic acid and 5-hydroxy-α,β-dipyridyl, characterized as the picrates.

4. It has been established that the methyl iodide is located on the nitrogen of the β-substituted pyridine ring in α,β-dipyridyl-5-nitrile.

5. The compounds which have been prepared are new and not described in the literature.

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COMPOUNDS OF NICOTINE WITH CUPRIC CHLORIDE AND CUPRIC BROMIDE

S. F. Babak and G. B. Kagramanova

In a preceding article [1], the synthesis of, and certain properties of, nicotine compounds with mercury chloride and bromide were described. The preparation and properties of compounds between cupric chloride and bromide and nicotine are described in the present work.

Amiel [2] upon dissolving nicotine hydrochloride in an aqueous solution of cupric chloride, and subsequently evaporating this solution, obtained bright-yellow crystals of the composition $[CuCl_4](C_{10}H_{14}N_2H_2) \cdot H_2O$. On dehydrating this compound, a dark-yellow compound of the composition $[CuCl_4](C_{10}H_{14}N_2H_2)$ was formed. The interaction of nicotine hydrobromide with cupric bromide in aqueous solution by the same authors produced lustrous black crystals of composition $[CuBr_4](C_{10}H_{14}N_2H_2)$.

The present authors have studied the interaction of cupric chloride with nicotine in acetone, and of cupric bromide with nicotine in ethyl alcohol.

EXPERIMENTAL

Commercial acetone and ethyl alcohol were doubly distilled. The nicotine, prepared from technical nicotine sulfate, boiled at 111-112° (6 mm), d_{25} 1.0068, η_{25} 3.8942. The cupric chloride and bromide used were chemically pure. The hydrochloric acid was purified by distillation.

$(CuCl_2)_2 \cdot C_{10}H_{14}N_2$. The compound was obtained as an amorphous yellow precipitate upon mixing acetone solutions in stoichiometric ratio of cupric chloride and nicotine (slight excess). The precipitate darkened in the presences of a trace of acetone and moisture of the air, and was therefore transferred quickly to a Schott filter covered with a stopper and calcium chloride tube and dropping funnel, washed several times with acetone and dried in a vacuum desiccator. The compound was in the form of a yellow powder, stable in air in the dry state. The yield of pure product was about 96% (melting with decomposition at 130-131°). Nitrogen was determined according to Dumas, nicotine determined by titration with sulfuric acid in the presence of methyl red, and after distilling twice from alkaline solution with steam, the halide was determined volumetrically according to Volhard, copper being determined iodometrically.

0.1352 g sub.: 0.1760 g AgCl. 0.1368 g sub.: 0.1752 g AgCl. 0.0174 g sub.: 0.0051 g Cu. 0.0202 g sub.: 0.0058 g Cu. 0.0986 g sub.: 6 ml N_2 (19°, 703 mm). 0.1428 g sub.: 8.6 ml N_2 (19°, 703 mm). Found %: Cl 32.15, 32.36; Cu 28.98, 29.05; N 6.57, 6.51. $(CuCl_2)_2C_{10}H_{14}N_2$. Calculated %: Cl 32.98; Cu 29.49; N 6.44.

The compound was readily soluble in water and dilute acids, very poorly soluble in chloroform and carbon tetrachloride, and insoluble in acetone, ethyl ether, ethyl alcohol, toluene and benzene.

$CuCl_2 \cdot C_{10}H_{14}N_2$. For preparation of this compound, cupric chloride and nicotine were taken in equimolecular amounts. As the nicotine was added to an acetone solution of cupric chloride, a beige-colored precipitate separated, changing to a green color, and finally fine, lustrous, brown crystals resulted, which were filtered, washed several times with acetone, and dried in a vacuum desiccator. The dry crystals were stable in air. Yield was 80%. Melting with decomposition at 120-121°.

0.1562 g sub.: 0.1514 g AgCl. 0.1499 g sub.: 0.1446 g AgCl. 0.0426 g sub.: 0.0092 g Cu. 0.0410 g sub.: 0.0090 g Cu. 0.1620 g sub.: 15.6 ml N_2 (29°, 700 mm). 0.1760 g sub.: 17 ml N_2 (30°, 700 mm). Found %: Cl 23.94, 23.82; Cu 21.54, 21.58; N 9.14, 9.42. $CuCl_2 \cdot C_{10}H_{14}N_2$. Calculated %. Cl 23.91; Cu 21.42; N 9.10.

The compound was insoluble in cold water, hydrolyzing in warm and hot water as with the preceding compound. Solubility was good in aqueous acid solution, but poor in chloroform and benzene. Solubility in benzene increased noticeably with increased temperature. Insoluble in acetone, ethyl ether, ethyl alcohol and toluene.

$2CuCl_2 \cdot 4C_{10}H_{14}N_2 \cdot 4HCl \cdot H_2O$. Dry hydrogen chloride was passed into a solution consisting of 1 g of cupric chloride and 40 ml of acetone until the dirty green color changed completely to red-brown, considerable spontaneous heat evolution being observed. After cooling the solution to room temperature, there was added dropwise 4 g of nicotine dissolved in acetone, with stirring. A milky-white solution and an oily liquid, dark-blue in color on the bottom of the flask, were formed. The oily liquid was separated and dissolved in a small amount of water. The resulting solution acquired a blue-green color. The solution was placed in a crystallizer, and after several days at room temperature, fine, blue, lustrous crystals were formed. The crystals were extracted, dried between sheets of filter paper, and then in a desiccator over calcium chloride. The yield was about 85%. The resulting compound was recrystallized from water. It melted with decomposition at 136°.

0.0938 g sub.: 0.1028 g AgCl. 0.1572 g sub.: 0.1798 g AgCl. 0.0452 g sub.: 0.0052 g Cu. 0.0264 g sub.: 0.0029 g Cu. 0.1578 g sub.: 16.2 ml N_2 (29°, 698 mm). 0.1061 g sub.: 9.8 ml N_2(18°, 703 mm). 0.3296 g sub.: 0.0050 g H_2O. 0.3602 g sub.: 0.0056 g H_2O. Found %: Cl 27.06, 27.30; Cu 11.34, 11.22; N 10.46, 10.26; H_2O 1.51, 1.51. $2CuCl_2 \cdot 4C_{10}H_{14}N_4 \cdot 4HCl \cdot H_2O$. Calculated %: Cl 26.27; Cu 11.75; N 10.26; H_2O 1.66.

Water determination was carried out by loss in weight of water on a portion of the compound, by heating to constant weight at 92°, whereupon the blue crystals became green. If left standing in air, however, they again acquired a blue color. The compound was readily soluble in water, forming a blue solution of acid reaction. It dissolved in ethyl alcohol but not in carbon tetrachloride, benzene, ethyl ether or acetone.

$CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$. This compound was prepared by Amiel by dehydrating the compound $[CuCl_4]$-$(C_{10}H_{14}N_2H_2) \cdot H_2O$ at 80°. It was synthesized by the authors from the anhydrous compounds in dry acetone medium. For this purpose, cupric chloride and nicotine were taken in equimolecular amounts. The acetone solution of cupric chloride was saturated with hydrogen chloride, whereupon considerable spontaneous heat evolution was observed. In order to prevent air moisture from getting into the solution, suitable precautionary steps were taken. After the solution was at room temperature, an acetone solution of nicotine was added to it dropwise, whereupon a bright-yellow, powdery precipitate separated. The precipitate was separated from the solution, washed several times with acetone and dried in a vacuum desiccator. Yield of the compound obtained was about 78%. It melted with decomposition at 140-143°.

0.1770 g sub.: 0.2772 g AgCl. 0.1486 g sub.: 0.2318 g AgCl. 0.0252 g sub.: 0.0046 g Cu. 0.0248 g sub.: 0.0045 g Cu. 0.1782 g sub.: 13.6 ml N_2 (29°, 700 mm). 0.1644 g sub.: 13 ml N_2 (30°, 698 mm). Found %: Cl 38.68, 38.53; N 7.79, 8.04; Cu 17.86, 18.04. $CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$. Claculated %: Cl 38.42; N 7.57; Cu 17.9.

The compound was readily soluble in water, the solution having a strong acid reaction. Solubility in acetone and ethyl alcohol was low. Insoluble in chloroform, ethyl ether, toluene and benzene.

The authors also repeated synthesis of the compound $CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl \cdot H_2O$, prepared by Amiel, and some of its properties which Amiel did not indicate in his work were determined. The compound resulted by interaction of equimolecular amounts of cupric chloride and nicotine in aqueous, strong hydrochloric acid medium, with subsequent crystallization of the product. Yield was 77%. It melted with decomposition at 129-130°. Orange-yellow crystals, readily soluble in water, with strongly acid reaction. The compound was readily soluble in 96% ethyl alcohol. Insoluble in carbon tetrachloride, benzene, toluene, ethyl ether and acetone.

$CuBr_2 \cdot C_{10}H_{14}N_2$. 4.8 g of nicotine, dissolved in alcohol, was added dropwise, with stirring, to a solution of 2.23 g cupric bromide and 50 ml of ethyl alcohol. Fine brown crystals separated and a blue-green solution resulted. The crystals were filtered off, washed with alcohol, and dried in a vacuum desiccator. The dry crystals were stable in air. Yield was about 77.7%. M.p. was 124.5-125°.

0.1782 g sub.: 13 ml N_2 (32°, 693.9 mm). 0.1778 g sub.: 13 ml N_2 (32°, 693.9 mm). 0.1508 g sub.: 0.0249 g Cu. 0.1482 g sub.: 0.0244 g Cu. 0.1500 g sub.: 0.0635 g Br_2. 0.1442 g sub.: 0.0603 g Br_2. 0.1482 g sub.: 0.0606 g Br_2. Found %: N 7.36, 7.37; Cu 16.55, 16.45; Br 41.10, 41.81, 40.84. $CuBr_2 \cdot C_{10}H_{14}N_2$. Calculated %: N 7.26; Cu 16.49; Br 41.46.

The compound was soluble in acids, hydrolyzing with water. It was poorly soluble in ethyl alcohol and benzene. It did not dissolve in carbon tetrachloride or ethyl ether. After separation of the compound $CuBr_2 \cdot C_{10}H_{14}N_2$, it was placed in a crystallizer, from which, after several days at room temperature, were formed silky-white, needle crystals. The crystals were separated from the mother liquor (blue-green in color), washed with ether, and air-dried. Yield was small, all told about 10%. M. P. was 137-140°. Repeated analysis of this compound indicated a composition of about 29.32% Br, 10.63% N, carbon and hydrogen present, but no copper. The compound dissolved in ethyl alcohol and acids, but was insoluble in carbon tetrachloride, ether and benzene.

Upon mixing alcoholic solutions of copper bromide and nicotine in the ratio of 1 : 1, the compound $CuBr_2 \cdot C_{10}H_{14}N_2$ immediately separated from solution. This compound was filtered, and from the filtrate after a period of time were formed fine, dark-red, crystals. The crystals were separated from the mother liquor, washed with alcohol, and dried. They were stable in air. Yield was negligible. M.p. was 245-246°. The compound was poorly soluble in alcohol and water. Solubility in nitric acid was good. Solubility was also good in a concentrated solution of sodium hydroxide, and a transparent, slightly-yellow solution was formed. Analysis indicated the presence of about 50% bromine, a high content of nitrogen, carbon and hydrogen being found, no copper being found in the compound. The last two compounds, not containing copper, whose quantitative composition have not yet been completely established, brings to mind the fact that copper bromide can brominate nicotine.

In studying the combination of nicotine with copper bromide and chloride, the latter's high reactivity should be mentioned. Depending upon conditions of the reaction course, they form several compounds with nicotine. There is the possibility of forming, under other conditions and solvents, compounds of copper bromide and chloride with nicotine of other compositions.

SUMMARY

1. A powdery compound of nicotine with copper chloride, of the composition $(CuCl_2)_2 \cdot C_{10}H_{14}N_2$, has been prepared.

2. Crystalline compounds of nicotine with copper chloride, of the composition $CuCl_2 \cdot C_{10}H_{14}N_2$; $2CuCl_2 \cdot 4C_{10}H_{14}N_2 \cdot 4HCl \cdot H_2O$, have been prepared.

3. A powdery compound of nicotine with copper chloride, of the composition $CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$, has been prepared (by a method differing from that known in the literature).

4. A crystalline compound of nicotine with copper bromide, of the composition $CuBr_2 \cdot C_{10}H_{14}N_2$, has been prepared.

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DISCUSSION

COMMENT ON THE ARTICLE BY A.A. BOLSHAKOVA:

INTERACTION OF METHYL-α-NAPHTHYLMERCURY AND METHYLPHENYLMERCURY WITH ORGANIC ACIDS

G. A. Razuvaev

In an article published recently by A. A. Bolshakova [1], the reactions of methyl-α-naphthylmercury and methylphenylmercury with a number of organic acids were described, which take place when the component is heated up to 75°. The reaction mechanism was presented by the following scheme:

$$CH_3HgR \rightarrow CH_3Hg\cdot + R\cdot$$

$$R\cdot + R'COOH \rightarrow RH + R'COO\cdot$$

$$CH_3Hg\cdot + R'COO\cdot \rightarrow CH_3HgOCOR'$$

Such an interpretation of the reaction mechanism appears to the commentor as entirely unsubstantiated, and very unlikely. Decomposition of metallo-organic compounds of mercury into radicals proceeds at temperature much above that of 75°.. Furthermore, the R radical should have removed the hydrogen atoms from the α-carbon atoms of the chain, and to a lesser extent, from the carboxyl [2]. Finally, were the R'COO radical to appear, it would have to have a sufficient half-life period, without decomposing, in order to encounter the CH_3Hg radical. In the meantime, it is to be expected that the R'COO radicals, which are now known in some detail, would decompose at 75° into R' and CO_2. Thus, for example, during reaction of acetyl peroxide or of benzoyl with mercury, the CH_3COO- and C_6H_5COO-radicals decompose completely into CO_2 and methyl- or phenyl-radicals at 80° [3].

At present, there is grave doubt that the free radical mechanism of reaction proceeds with formation of a CH_3COO- radical without the evolution of CO_2; for example, the oxidation reaction of β-glycols with lead tetraacetate [4], or certain reactions of the nitrosoacylarylamines [5]. However, the decomposition of lead tetraacetate in acetic acid to form CH_3COO- radicals, proceeds with evolution of CO_2 and methane [6]. It is not understood why the author considers the methyl radical to be less reactive than the naphthyl or phenyl radicals. On the contrary, it is known that the most reactive is the non-stabilized methyl radical.

It should be considered that the interaction of metallo-organic compounds of mercury with acids proceeds along the line of an ionic mechanism, similar to their reaction with hydrogen chloride; it is therefore natural to expect complete coincidence in sequence of radical rupture by the Kharasch order, as was indicated in the aforementioned work.

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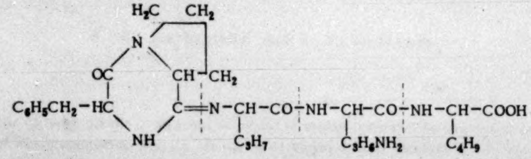
REGARDING THE STRUCTURE OF GRAMICIDIN C

M. S. Reznichenko

A recently-published paper by P. G. Ioanisiani, N. I. Gavrilova and M. O. Plekhan, "The Structure of Gramicidin C" [1] advances an arbitrary modification of the well-demonstrated formula of gramicidin C (p.371)*. According to the assertion of these authors, the structure is characterized by the presence of a diketopiperazine heterocycle and a free saturated carboxyl group



which is, however, not substantiated by any of the experimental data in the given work. Careful study of the material in this paper makes clear that the structure of gramicidin C advanced by the authors does not follow from the data they adduce, as is evident from the following.

1. The data of the paper in question completely lack any analytical evidence to support the presence in native or regenerated gramicidin of piperazine (or its derivatives) or of any quantity whatever of free carboxyl groups, which is in basic contradiction to the open structure the authors ascribe to gramicidin, which in reality is a cyclic polypeptide compound [2].

2. Table 1 (p. 373)* of the work in question adduces data testifying to a sharp increase in the quantity of amine nitrogen in the regenerated gramicidin preparation, attaining 130 to 350% of its original content. This increase in amine nitrogen does not stand (and cannot stand) in any causal relationship, as the authors believe (p. 374)* to the presence of heterocyclic groups in the structure ascribed to gramicidin. The fact of increase in amine nitrogen content, titrated by the Sörensen method or determined by the Van Slyke gasometric method, only demonstrates that gramicidin subjected to the conditions of experiment for a long period of time (more than 7 hours) in a mixture of concentrated hydrochloric and acetic acids (p. 372)* underwent hydrolysis (at the broken line on the adduced formula).

3. According to current biochemical concepts, the degree of hydrolysis of albuminous susbtances is practically controlled precisely by the quantity of increasing amine nitrogen. This being the case, the conclusion by Ioanisiani, Gavrilov and Plekhan that they had "demonstrated the presence in gramicidin C of two fragments of diketopiperazine and tripeptide" (p. 375)* on the basis of the observed rise in amine nitrogen, remains unsupported.

4. The method employed by these authors of electrical regeneration of peptides (and albumins) dissolved for this purpose in a mixture of concentrated hydrochloric and acetic acids, is defective. Aside from the fact that so powerful a reagent is itself capable, in several hours time, of causing hydrolysis of the peptide substance under study, its action causes, in reality, an even more profound change in the chemical nature of gramicidin. This conclusion is obvious upon examination of the data advanced on p. 373*, where the authors note that after the electrical regeneration of gramicidin, it was impossible to find in its hydrolysis products two (of the total number of five) of its proved decomposition products: phenylaniline and proline.

5. The use of the method of research employed by the authors for the study of gramicidin cannot serve as an objective criterion for determining the nature of its internal structure, as it undergoes profound destructive changes under the given conditions of experiment. The diketopiperazine-amidine structure ascribed to gramicidin by Ioanisiani, Gavrilov and Plekhan, being completely unsubstantiated, must be taken as fictitious and not reflecting the true nature of gramicidin C.

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* The indicated pagination is that of the C.B. Translation.

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• See Consultants Bureau English translation, page 371.

THE BEHAVIOR OF MAGNESIUM IN POTASSIUM DICHROMATE SOLUTIONS

A. G. Samartsev and E. I. Levitina

The active behavior of magnesium in aqueous solutions of electrolytes can be explained on the basis of its belonging to the group of electronegative metals. Passivity of magnesium is observed in alkaline solutions [1], as well as in chromate and fluoride salt solutions, in which layers of poorly-soluble compounds are formed at the magnesium surface.

Upon heating magnesium in potassium dichromate solution to the boiling point, there is observed after several minutes of immersion a small evolution of gaseous hydrogen, which subsequently ceases. The metal surface undergoes no noticeable changes upon further and prolonged standing in the solution. Under such conditions, the magnesium becomes passive, being covered with a thin protective layer.

Introduction into the potassium dichromate solution of some neutral salts which do not affect the acidity of the solution affects markedly the behavior of the metal: magnesium begins to dissolve extensively, hydrogen being displaced, and a visible protective layer is formed on the surface. Thus, under the influence of neutral salts, the metal surface becomes activated.

Up to the present time, this phenomenon has received but little study, although it has been known for a long time [2]. Introduction of activating salts into potassium dichromate solution is used widely in technology for the production of protective layers upon magnesium and its alloys [3].

In the present work, the growth rate for the protective layers on magnesium in potassium dichromate solution containing additives has been studied.

For the experiments, samples of pure magnesium (99.96%) in the form of sheets were used. The surface of one sample amounted to 30 cm². Experiments were carried out with 10% potassium dichromate solution, in which were introduced neutral salts as activating additives. The weight of layer produced was determined. Weighings were carried out on an analytical balance to within an accuracy of 0.1 mg. To determine the layer weight, the latter was removed from the sample by dissolving in concentrated alkali at elevated temperature. The solution, containing 600 g sodium hydroxide/liter, was used at the boiling temperature (125°). Soaking time of the metal in the solution was 30 seconds. Experiments indicated that by such procedure any error due to removal of the layer, apparently by dissolution of the metal, can be ignored. For coatings weighing 5-10 mg the error of determination did not exceed 5%.

In Fig. 1 is given the weight of coating used, as formed on magnesium in 10% potassium dichromate solution, versus the concentration of sodium sulfate introduced into solution. Experiments were carried out at 80°. As shown by measurements carried out with a glass electrode, the acidity of the solution did not change upon introduction of sodium sulfate.

In pure potassium dichromate solution under the same conditions, no coatings visible to the eye were formed on the metal, and samples of the metal did not change in weight. Upon introducing sodium sulfate, a violent evolution of hydrogen from the metal surface of the sample was observed. Light-brown non-uniform coatings were formed on the metal surface in solution containing 5 g of sodium sulfate/liter. With increased concentrations of sodium sulfate, up to 20 g/liter and higher, the resulting coats were of uniform dark-brown color.

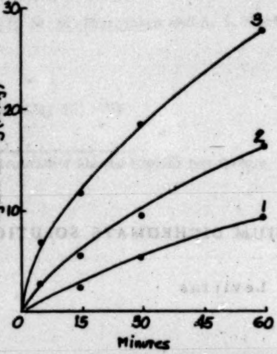

Fig. 1. Effect of activating additive (sodium sulfate) upon protective coating growth on magnesium in 10% potassium dichromate solution. Temperature of solution, 80°. 1) 5 g/l Na_2SO_4; 2) 20 g/l Na_2SO_4; 3) 100 g/l Na_2SO_4.

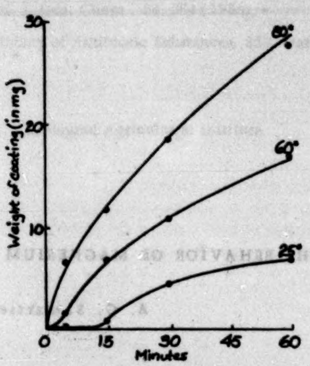

Fig. 2. Effect of activating additive upon the growth of protective coating on magnesium in 10% potassium dichromate solution relative to temperature. Solution containing 100 g sodium sulfate per liter.

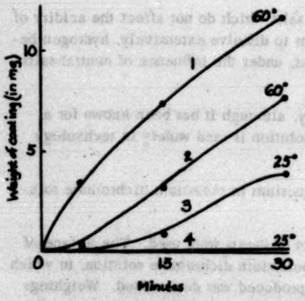

Fig. 3. Protective coating growth on magnesium in 10% potassium dichromate solution with respect to metal surface condition. Solution containing 100 g sodium sulfate/liter. Temperatures, 60 and 25°. 1, 3) Polished samples without added chemical processing; 2, 4) samples pretreated in potassium dichromate solution.

With increase in time, the rate of growth of the coating decreased. The process thus possessed a decelerating character. The coating formed apparently inhibits the rate of chemical reaction between metal and solution.

Analogous phenomena were observed with the chlorides, phosphates and fluorides of the alkali metals introduced into the potassium dichromate solutions. In potassium dichromate containing chlorides, coating formation is accompanied by centers of disintegration of the metal. In solutions containing phosphate, the coating increased at a lower rate than for solutions containing sulfates. The action of fluoride salts depended upon their concentration in the solution. Addition of small amounts of fluoride (0.1 g sodium fluoride/liter) acted in a manner similar to that for sulfate and phosphate salts; in such cases, metal surface coatings of considerable thickness were formed, brown in color. With an increased content of fluoride, however, there were formed colorless coatings of magnesium fluoride on the metal. Evolution of hydrogen on the metal sample ceased rapidly in this case.

The effect of activating additives depends considerably upon the acidity of the potassium dichromate solution. The rate of metal solubility decreases sharply with decrease in acidity, and hence the rate of coating growth is slowed down.

The temperature of the solution exerts a great influence upon the coating growth. Corresponding data for 10% potassium dichromate solution, containing 100 g sodium sulfate per liter, are given in Fig. 2. Experiments were carried out at 25, 60 and 80°.

As can be seen from Fig. 2, the rate of growth of protective coating decreases with decrease in temperature of solution. There was observed at lower temperature an induction period in coating formation during initial stages of the process. It was most evident at 25°. The induction period is apparently related to the presence of a natural oxidation layer on the metal surface.

The rate of coating growth on magnesium in potassium dichromate solution containing sodium sulfate (at pH 3.2) decreases sharply if the metal sample is suspended beforehand in potassium dichromate solution heated to boiling and without additives. The experimental data are presented in Fig. 3. If experiments are carried out at 25°, then complete passivation of metal is observed, no visible coating being formed in this case (Curve 4). For samples not pretreated in dichromate, there appears, as was indicated, a relatively thick layer. The marked effect of preliminary passivation (Curves 1 and 2) is clearly observed at 60°; it is first of all expressed by the presence of an induction period during the initial stage of coating growth. Preliminary passivation was carried out in 10% potassium dichromate solution by boiling for 30 minutes.

Thus magnesium was found to be passive in solutions of potassium dichromate even at boiling temperature: on the surface is formed a thin invisible passivity-inducing layer, which appears during the induction period in the above-described experiments.

An explanation for the action of the activating salt should be sought for in the fact that for anions of these salts the film forming is found to be permeable. Dissolution of metal is the consequence, accompanied by violent evolution of hydrogen and by growth in thickness of the film.

The ability of various anions to penetrate through the protective layer of metals has received but little study. It has been established that chloride ions possess high permeativity [4].

The growth mechanism for the protective layer on magnesium in chromate salt solutions can be schematically presented as follows. The magnesium going into solution reduces the hexavalent chromium to trivalent. The solution is rendered alkaline in the area of the metal surface, and trivalent chromium compounds of low solubility separate from solution, forming a protective layer on the metal surface. Magnesium as well as hexavalent chromium can enter into the composition of the film. In the process of coating growth, part of the metal becomes lost to the solution and does not participate in construction of the coating.

SUMMARY

1. Magnesium is rendered passive in potassium dichromate solutions, both at room temperature and at the boiling point. Passivity is conditioned by the formation of a thin, invisible, protective coating, composed of poorly-soluble compounds.

2. Introduction of "activating" salts into the solution partially destroys passivity of the metal, and leads to formation of a surface layer of considerable thickness, varying in color from yellow to brown.

3. The effect of activating salts depends in great part upon the temperature and acidity of the solution.

4. Activation of the salts introduced is apparently connected with the permeability of the protective layer to anions of these salts.

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Received May 13, 1954.

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THE THERMAL EFFECT OF THE $PBCl_2$ (cr) + Cl_2(g) $\rightleftharpoons$ $PbCl_4$(liq) REACTION AND THE STANDARD HEAT OF FORMATION OF $PbCl_4$(liq.)*

F. Ya. Kulba

Many investigators have attempted in vain to prepare $PbCl_4$ by direct oxidation of lead chloride with chlorine under various conditions. In the author's preceding article [1], lead tetrachloride was characterized from a chemical viewpoint. Desiring to study in detail the conditions for formation of this compound, the authors decided to measure its heat of formation from lead chloride and chlorine, and to calculate the standard heat of formation for $PbCl_4$ (liq.) from elementary substances.

As the basis for thermochemical measurements, the interaction of lead tetrachloride with excess iodine dissolved in carbon tetrachloride was used.

EXPERIMENTAL

1. Selection of Calorimeter System and Accuracy of the Measuring Apparatus

The stability of lead tetrachloride and its solutions prepared by suitable procedure (in CCl_4) at 25° made it possible for the authors to carry out the thermochemical measurements under standard conditions.

Allowing for the fact that preliminary experimental results indicated for orientation that the reactions $PbCl_4$ (liq.) + I_2 (sol.) $\rightarrow$ $PbCl_2$ (cr.) + 2 ICl (sol.), and I_2 (sol.) + Cl_2 (g) $\rightarrow$ 2 ICl (sol.), under investigation, are accompanied by a considerable thermal effect, the author decided to select for his calorimeter system the standard calorimeter of Boze-Vrevsky, described in the works of Vrevsky [2], Mischenko, and other investigators [3, 4, 5].

As calorimeter container, a thin-walled, glass beaker, 405 ml in volume, served. Its ratio of height to diameter was 1.4. The calorimeter cover was made of "textilite" plastic, 0.5 mm in thickness. The measuring instruments (Beckmann thermometer, milliammeter, and millivoltmeter) were checked beforehand. Accuracy of temperature readings amounted to ± 0.001° C. Amperage and voltage were, respectively, measured to within an accuracy of ± 0.005 A and ± 0.002 V. Accuracy of the secondmeter was ± 0.2 sec.

2. Reaction Cycle

Being unable to carry out in the calorimeter a direct synthesis or decomposition of lead tetrachloride, the heat of formation was determined according to the following cycle:

$$\begin{tikzcd}
PbCl_4\,(liq.) + I_2\,(sol.) \arrow[rr, "\Delta H^0"] & & PbCl_2\,(cr.) + 2ICl\,(sol.) \arrow[dl, "\Delta H_1^0"] \\
& PbCl_2\,(cr.) + I_2\,(sol.)\ Cl_2\,(g.) \arrow[ul, "-2\Delta H_2^0"] &
\end{tikzcd}$$

According to the law of Hess:

$$\Delta H^0 + \Delta H_1^0 - 2\Delta H_2^0 = 0.$$

Hence,

$$\Delta H^0 = 2\Delta H_2^0 - \Delta H_1^0.$$

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* Throughout the article, the following abbreviations are used: cr. = crystalline, g. = gas, liq. = liquid, sol. = solution.

Thus, to calculate the thermal effect of interest to us, the heats of reaction given in the cycle under standard conditions had to be measured:

$$PbCl_4\,(liq.) + I_2\,(sol.) \rightarrow PbCl_2\,(cr.) + 2ICl\,(sol.) + \Delta H_1^{0}$$

and

$$Cl_2\,(g.) + K_2\,(sol.) \rightarrow 2ICl\,(sol.) + 2\Delta H_2^{0}.$$

3. Procedure for Measuring the Heat of $PbCl_4$ (liq.) + I_2 (sol.) → $PbCl_2$ (cr.) + + 2ICl (sol.) Reaction

Since introduction of lead tetrachloride in solution into the calorimeter container is difficult from the point of view of isothermicity of the solutions mixed, the author preferred to introduce $PbCl_4$ in the free state, particularly since the high thermal effect of the reaction makes it possible to neglect such a small amount. Difficulty remained only in the fact that because of instability of the lead tetrachloride in air, it could not be introduced into the calorimeter by ordinary procedure.

After a number of preliminary experiments, the author decided to use for this purpose an apparatus shown in the drawing, consisting of a U-shaped pipette, 3 ml in volume, a small funnel, and a cylindrical glass tube, the top internal wall of which was ground. The funnel was equipped with a long outlet tube reaching almost to the surface of the solution in the calorimeter, and serving at the same time as a stopcock for the cylindrical tube. Its external conical wall was ground and firmly sealed the tube opening. The upper part of the funnel was cylindrical and fitted tightly to the ground tube.

The cylindrical glass tube with funnel placed inside was vertically and tightly fitted into the opening of the calorimeter cover. In assembled form, together with the funnel, it was of such height as to protrude above the upper calorimeter wall not more than 1-1.5 cm. By such an arrangement of the apparatus, the walls of the funnel possessed, at the moment of thermal equilibrium of the system, the temperature of the calorimeter casing, because of which fact heat exchange with lead tetrachloride at its moment of introduction into the calorimeter was avoided. Prior to start of the experiment, the lead tetrachloride (2), introduced into the pipette and covered with a film of concentrated sulfuric acid (1) (Fig. 1), was placed in a thermostat, in which it was heated to the experimental temperature (25° C). At the proper time, the pipette was removed from the thermostat, and the upper layer of sulfuric acid along with a small amount of $PbCl_4$ was decanted off from the tube placed at an angle. Immediately following this operation, the lead tetrachloride remaining in the pipette was poured through the funnel into the calorimeter beaker with iodine solution (12 g of iodine per liter of solution), but a small amount together with the sulfuric acid layer at the top was left in the pipette to avoid getting acid into the reaction mixture. The funnel was immediately removed subsequent to the operation, since otherwise the lead tetrachloride remaining on the wall would disintegrate, by such action disturbing the normal temperature course in the final experimental phase. After removal from the funnel, the tube was immediately covered with a ground stopcock.

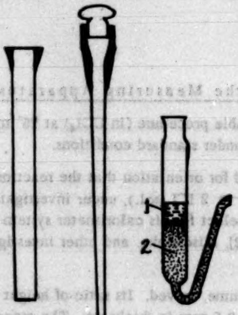

Fig. 1. Apparatus for introduction of $PbCl_4$ into calorimeter. Explanation in text.

Each determination of thermal effect consisted actually of two separate experiments: an elevation in temperature was first measured corresponding to a specific amount of $PbCl_4$ reacting with the iodine, and then after cooling the calorimetric beaker contents, the temperature rise corresponding to a specific quantity of electrical energy passed through the mercury spiral measured. The quantity of lead tetrachloride entering into reaction was found each time by analysis according to the sulfate method, after having taken the calorimetric measurements.

4. Calculation of the thermal Effect of the Reaction Carried out According to the Formula $\Delta H^0_{298} = \frac{Q \cdot m \cdot \Delta\theta}{a \cdot \Delta T}$

where ΔH^0_{298} is the heat of reaction, calculated for 1 mole;

m is the molecular weight of $PbSO_4$, equal to 303.28;

a is the weight of lead sulfate found analytically;

$\Delta\theta$ is the temperature rise at expense of heat evolved during reaction time;

ΔT is the temperature rise while heating the calorimeter contents by electric current;

Q is the quantity of heat (in calories) given up by the mercury spiral during passage of the electric current.

The data obtained by the author are presented in Table 1.

TABLE 1

Thermal Effect of the Interaction of Lead Tetrachloride with Iodine Dissolved in Carbon Tetrachloride

Indicators	Symbols	Experiment No.				
		1	2	3	4	5
Weight of iodine solution	B	499.7	499.8	499.7	498.5	499.1
Weight of $PbSO_4$	a	2.0804	2.2507	2.4181	2.1726	2.3391
Temperature rise.	$\Delta\theta$	1.157	1.228	1.323	1.195	1.281
Correction for radiation during reaction . . .	$\Delta(\Delta\theta)$	0.031	0.039	0.032	0.028	0.027
Temperature rise.	ΔT	1.425	1.003	1.021	0.975	0.991
Correction for radiation during passage of electric current through spiral	$\Delta(\Delta T)$	0.050	0.020	0.020	0.013	0.030
Amperage	I	2.8040	2.8980	2.9138	2.8396	2.8580
Voltage.	E	2.8126	2.8980	2.9225	2.8405	2.8614
Duration of current flow (in sec.)	t"	90.2	60.2	60.4	60.6	60.6
Quantity of heat (in calories) evolved during the experiment, due to the reaction.	Q	168.47	119.74	121.81	115.76	117.36
Thermal effect of the reaction.	ΔH^0_{298}	−19941*	−19754	−19795	−19805	−19672
Average value	ΔH^0_{298}			−19793 cal/mole		
Average absolute error	$\Delta(\Delta H^0_{298})$			± 64 cal/mole		
Average relative error	—			—	± 0.32%	

5. Procedure and Results of Measurements of Heat of Formation of Iodine Chloride From Gaseous Chlorine and Iodine Dissolved in Carbon Tetrachloride

a) Starting products. The iodine solution was prepared of same concentration as in preceding measurements, i.e., 12 g of iodine per liter of solution. After preparation of the solution, the iodine concentration was determined accurately by titration. The iodine and carbon tetrachloride were purified thoroughly each time.

Chlorine was taken from a tank, but was first passed through tubes of concentrated sulfuric acid to absorb moisture. Chlorine dried in this manner was analyzed to determine the total impurities in it (CO_2, N_2, CO, O_2), collectively, since under the author's experimental conditions none of the separate components could interact chemically with the calorimeter contents, and could only cause an undesirable change of enthalpy in the system upon passing through the solution (due to evaporation of carbon tetrachloride).

The total impurities not absorbed by 10% KI solution constituted on the average (three measurements) 0.2 ml for 132.5 ml of chlorine, or 0.15% (burette for the analysis graduated with mercury). Since approximately 200 ml of chlorine was introduced into the calorimeter during the experiment, the volume of unabsorbed gases, therefore, can be considered equal to $200.0 \cdot 0.0015 = 0.3$ ml, and the volume of carbon tetrachloride evaporated by same to be even less. The quantity of heat used by the system for this evaporation was beyond the range of accuracy of the calorimetric measurements, because of which errors from these heat losses were not introduced.

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* Exothermal effect is —; endothermal effect is +.

b) Apparatus for introducing chlorine into the calorimeter. It was established by preliminary experiments that in order to produce an increase of 1° in temperature at the expense of the reaction, it is necessary to introduce about 200 ml of chlorine into the calorimeter.

It was not feasible in the case of the calorimeter, however, to set up a container of such volume directly in the calorimeter beaker or in the calorimeter case; the author, therefore, constructed the apparatus in such manner that it permitted carrying out of chlorine preheating to the experimental temperature of the thermostat. It was borne in mind, however, that the exact quantity of chlorine entering into reaction is determined not by direct measurement of its volume in the apparatus, but by titration of the calorimeter contents after the experiment.

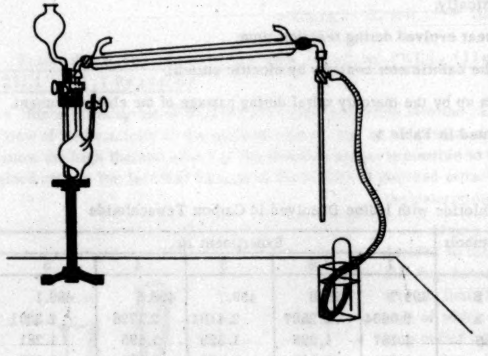
Fig. 2. Apparatus for heating chlorine prior to its introduction into the calorimeter. Explanation in text.

The main part of the apparatus (Fig. 2) consisted of two round glass containers inter-connected by a glass tube of about 0.4 cm diameter. The upper outlet tube of the bottom container consisted of a thick-walled capillary, ending at the top with a ground exterior. The outlet tube was closed by a three-way stopcock, and the connecting tube by a standard stopcock. The lower container was filled with chlorine before the experiment, the upper reserved for concentrated sulfuric acid, by means of which chlorine was displaced from the lower container to the calorimeter. The outlet tube of the lower container was connected by a ground surface to the capillary tube bent at a 90° angle, which in its turn was also connected by a ground surface to the container full of chlorine, with a thin-walled capillary tube immersed in the calorimeter solution and fastened to the cover of the latter. The calorimeter tube was closed at its upper part by a three-way stopcock and was ground at the top. The tube connecting container with calorimeter was placed in a glass sleeve, through the inside of which circulated water, entering from the calorimeter case into the thermostat. The container with chlorine was fastened in such way that it could be freely rotated in any direction, which made it possible to set the openings of the ground stopcock in that position which allowed hermetic connection with the bent tube which was slipped on from above.

The container was filled with chlorine in the upturned position. The chlorine which entered through the outlet tube displaced the air rapidly and completely. (Complete displacement of air was checked with KI.) The stopcocks closing the container were closed with continuous chlorine flow, in such sequence that the three-way stopcock was the last to be closed.

The temperature at which the container was filled with chlorine was approximately 5° below the thermostat temperature.

Because of this fact, chlorine before the start of the experiment was heated in a thermostat at 25° C (temperature tested by thermometer placed inside container with chlorine) and was at all times under some pressure, which served to effect automatic displacement of air from the horizontal tube connecting chlorine-filled container with calorimeter. It was done as follows. Before start of the experiment, the three-way stopcock of the tube lowered into the beaker with solution was set in such a way that the end of the tube was connected with the outlet of the horizontal connecting tube, and through a second three-way stopcock, to the air. Chlorine in the container, which was under a slight pressure at this time, escaped outside and displaced air from the tubes in the space between the two three-way stopcocks. Since, along with air, a small amount of chlorine also escaped, to avoid pollution of the surrounding atmosphere the authors led this mixture of gases (chlorine and air) into a pneumatic bath through a tube connected with the side outlet of the tap. Thus heat losses were avoided which would have inevitably taken place as a result of carbon tetrachloride evaporation while passing through a solution of the air trapped in the tubes.

The chlorine was introduced into the carbon tetrachloride solution of iodine (in the calorimeter), together with an 11th reading of the temperature from start of the experiment. During the time interval between 10th and 11th readings of temperature concentrated sulfuric acid was poured into the upper container which had been in the thermostat for one hour prior to this operation. Immediately after pouring in the sulfuric acid, the three-way stopcock was turned in such manner that chlorine escaping from the container could be directed into the calorimeter. Simultaneously with the 11th reading of temperature, the stopcock in the lower part of the container with sulfuric acid was opened. The latter flowed evenly into the lower part of the container with chlorine, displacing it gradually into the calorimeter.

Inflow of chlorine into calorimeter was interrupted at the desired moment by an appropriate turn of the three-way stopcock.

The amount of heat corresponding to the temperature rise upon passing a specific amount of chlorine into the calorimeter was found similarly as for the heat effect measured in the first reaction.

c) Analytical method and results of measurements. The amount of chlorine interacting with iodine, and hence the amount of iodine chloride formed, was determined by titration with sodium thiosulfate. In this connection, interaction of chlorine with iodine proceeded in excess of the latter, and in the analyzed solution iodine and iodine chloride were present together. Their quantities were determined by difference of two titrations of one and the same iodine solution, before and after introducing chlorine. Since each iodine molecule during titration used twice as much sodium thiosulfate as for 1 atom of free iodine, the increase in volume of $Na_2S_2O_3$ solution therefore, was recalculated to the number of gram atoms of iodine corresponding to the number of moles of iodine chloride formed. The solution was analyzed immediately after termination of the experiment by means of three parallel determinations. Samples of the solution were taken by pipette (with three-way stopcock, 25 ml volume) directly from the calorimetric beaker while still closed — through an outlet in the calorimeter. The solution in the pipette was poured into a flask with potassium iodide dissolved in 25 ml of water. Since the flasks with KI had been weighed beforehand, after a second weighing, the solution was analyzed, and sample weights determined. Because of the fact that the iodine solution was taken in weight units and not volume units for the experiment, as the final weight of sample analyzed there was taken the weight after deducting the chlorine which was passed into the sample and reacted. After weighing, the solution was immediately diluted with water and titrated with sodium thiosulfate solution.

Calculation of the thermal effect for the reaction, on the basis of data obtained, was carried out (Table 2) in a manner similar to that which was carried out in determination of the heat of interaction of lead tetrachloride with iodine:

$$\Delta H^0_{298} = \frac{Q \cdot \Delta\theta}{\Delta T \cdot n} = \frac{Q \cdot \Delta\theta \cdot 1000}{\Delta T \cdot B \cdot \frac{V_2 V_1}{b_1 - a} \quad N}$$

6. Heat of Formation of Lead Tetrachloride from Crystalline Lead Chloride and Gaseous Chlorine

From the reaction cycle given above, it follows that the heat of formation of lead tetrachloride from crystalline lead chloride and gaseous chlorine (ΔH^0) is: $\Delta H^0 = 2\Delta H_2^0 - \Delta H_1^0$, where ΔH_2^1 is equal to the heat of formation of one mole of iodine chloride and ΔH_1^0 is equal to the heat of interaction of one mole of lead tetrachloride with iodine.

Replacing ΔH_2^0 and ΔH_1^0 values we find that

$$\Delta H^0 = 2.6395 + 19793 = +7003 \text{ cal/mole}$$

Taking into account the average absolute and maximum absolute error, the final outcome is

$$PbCl_2 \text{ (cr.)} + Cl_2 \text{ (g.)} \rightarrow PbCl_4 \text{ (liq.)} + 7003 \pm 76 \text{ cal/mole and}$$

$$+ 7003 \pm 256 \text{ cal/mole.}$$

TABLE 2

Heat of Formation of Iodine Chloride from Gaseous Chlorine and Iodine Dissolved in Carbon Tetrachloride

Index	Symbol	Experiment No.			
		1	2	3	4
Weight of iodine solution	B	498.40	498.40	498.35	498.48
Results of analysis	$\frac{V_1}{a}$	0.6051	0.6051	0.6051	0.6073
	$\frac{V_2}{b_1}$	1.0179	1.0115	1.0193	1.0205
	$\frac{V_2}{b_1} - \frac{V_1}{a}$	0.4128	0.4064	0.4142	0.4132
Normality of sodium thiosulfate solution	N	0.09773	0.09773	0.09773	0.09773
Temperature rise	$\Delta\theta$	1.093	1.068	1.100	1.091
Correction for radiation during reaction	$\Delta(\Delta\theta)$	+0.0003	+0.0110	+0.0080	+0.0040
Temperature rise	ΔT	0.996	1.026	0.963	1.001
Correction for radiation during passage of electric current through spiral	$\Delta(\Delta T)$	+0.028	+0.031	+0.032	+0.026
Amperage	I	2.7651	2.7568	2.7199	2.7508
Voltage	E	2.7820	2.7730	2.7400	2.7680
Duration of current passage (in seconds)	t"	64.4	66.4	64.0	65.4
Quantity of heat (in cal.) evolved during reaction	Q	117.32	120.43	112.96	117.94
Thermal effect of reaction	ΔH^0_{298}	−6403	−6333	−6396	−6386
Average value for thermal effect	ΔH^0_{298}	−(6403 + 6396 + 6386) : 3 = 6395 cal/mole			
Average absolute error	$\Delta(\Delta H_{298})$	± 6 cal/mole			
Average relative error	—	0.1%			

TABLE 3

Heat of Dissolution of Lead Tetrachloride in Carbon Tetrachloride

Index	Symbol	Experiment No.			
		1	2	3	4
Weight of CCl_4 taken for the experiment	B	493.63	493.98	494.28	494.18
Weight of sample analyzed	b	39.96	39.95	39.98	39.85
Weight of $PbSO_4$, separate sample	a	0.8685	0.7597	0.7411	0.5480
Weight of $PbCl_4$, separate sample	c	0.9996	0.8744	0.8530	0.6307
Weight of CCl_4, separate sample	(b−c)	38.960	39.076	39.127	39.230
Concentration of solution	$\frac{PbCl_4}{CCl_4}$	$\frac{1}{1121}$	$\frac{1}{1282}$	$\frac{1}{1315}$	$\frac{1}{1778}$
Temperature drop	$\Delta\theta$	−0.215	−0.191	−0.190	−0.127
Correction for radiation during dissolution	$\Delta(\Delta\theta)$	−0.002	+0.001	0.000	+0.001
Temperature rise	ΔT	0.293	0.256	0.305	0.349
Correction of radiation during passage of electric current through spiral	$\Delta(\Delta T)$	+0.008	+0.009	+0.012	+0.015
Amperage	I	2.8235	2.7170	2.680	2.665
Voltage	E	2.810	2.722	2.683	2.676
Duration of current flow (in seconds)	t"	18.4	17.0	21.0	24.6
Thermal effect of dissolution (in cal.)	ΔH_m	699.2	701.5	718.3	664.2
Average value	ΔH_m	(699.2 + 701.5 + 718.3) : 3 = 706.7			
Average absolute error	—	± 8.1 cal/mole			

7. Standard Heat of Formation of $PbCl_4$ (liq.) from Elementary Substances

From the literature available [6], the standard heat of formation for $PbCl_2$ (cryst.) is equal to − 85.85 kcal/mole. Using these data, the standard heat of formation is found.

$$\underset{-85.85}{PbCl_2\ (cr.)} + \underset{0}{Cl_2\ (g.)} \rightarrow \underset{\Delta H^0_{PbCl_4\ (liq.)}}{PbCl_4\ (liq.)} + 7.0\ kcal/mole$$

According to the law of Hess $\Delta H^0_{PbCl_4\ (liq.)} = 7.0 - 85.85 = -78.85$ kcal/mole. Consequently:

$$Pb\ (cr.) + 2Cl_2\ (g.) \rightarrow PbCl_4\ (liq.) - 78.85\ kcal/mole.$$

8. Heat of Dissolution of Lead Tetrachloride in Carbon Tetrachloride

In order to study the nature of lead tetrachloride, and its behavior in carbon tetrachloride its heat of dissolution in the solvent indicated was carried out.

So far as procedure for measurements are concerned, the method for introducing carbon tetrachloride into the calorimeter and the course of analysis, these were carried out essentially as was done in determination of the heat of interaction for lead tetrachloride with iodine. It was necessary, however, to shorten to a considerable degree the duration of the experiment, since lead tetrachloride when dissolved in carbon tetrachloride decomposes on prolonged standing in the calorimeter. Because of this fact, following the final period corresponding to dissolution of $PbCl_4$, the author, rather than cooling as was done in the preceding experiments, passed an electric current through the solution. Thus, the final stage of the experiment, during dissolution of $PbCl_4$ was at the same time the initial period of the experiment during passage of the electric current.

The first part of the experiment by such a method proceeded normally, and the end of the main experiment corresponded, within the limits of accuracy of measurement, to a standard temperature of 25° C. However, during the course of the second part of the experiment, a known error was introduced: the average temperature rise during passage of the electric current did not correspond to 25° C, but was approximately 0.1° higher. However, from the quantitative side the error had no important influence since, due to a small rise in temperature with fluctuations of about 0.2°, the deviation in average temperature rise from 25° amounted to about 0.1°, and with a small temperature coefficient for dissolution in CCl_4 the results of measurement could not be greatly affected.

The amount of lead tetrachloride introduced into the calorimeter was as follows: the above-described funnel by means of which the $PbCl_4$ was introduced into the calorimeter was moistened beforehand with concentrated sulfuric acid. Without this seemingly insignificant operation, the experiments would not be successful. Very strong turbidity in the solution was noted in the beaker, as well as the formation of $PbSO_4$ precipitate. This once again gave evidence of the extreme sensitivity of lead tetrachloride to moisture.

The quantity of lead tetrachloride introduced into the calorimeter was determined by analysis of the solution after the experiment. For such purpose, a sample removed from the calorimeter was introduced into the carbon tetrachloride solution of iodine. The amount of lead chloride formed in this case was then determined by the usual gravimetric procedure according to the sulfate method.

The thermal effect of dissolution for (ΔH_m) per mole of $PbCl_4$ was found from the equation

$$\Delta H_m = \frac{0.2389 I \cdot E \cdot t'' \cdot 0.9913 \cdot \Delta\theta \cdot 349.05}{\Delta T \cdot A^{*}}\ \text{cal.}$$

or after replacing A by its corresponding values:

$$\Delta H_m = \frac{0.2389 I \cdot E \cdot t'' \cdot 0.9913\ \Delta\theta\ (b-c)\ 303.28}{\Delta T \cdot B \cdot a}\ \text{cal.}$$

All data for thermochemical measurements are given in Table 3.

Although in the first three experiments the extent of dissolution increased with dilution, in the fourth experiment, when dilution was greatest, it reached its lowest value. This can be explained either by a lower accuracy of measurements or by some peculiarity in the course of the curve in the range of the highest dilutions.

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* A = weight of $PbCl_4$ taken for experiment.

Since a study of this problem was not contemplated by the author, it was therefore decided to reject the results of the last experiment.

The result obtained is in agreement with the natures of both substance and solvent. In fact, the symmetry of the CCl_4 molecule (dipole moment equal to zero) and the slight polarity of the $PbCl_4$ molecule exclude possibility for formation of any compounds in the solution with any marked change in reserve energy. It can also be postulated that during dissolution there occurs a disrupting process of weakly-associated lead tetrachloride molecules, accompanied by negligible energy absorption.

Taking into account the average absolute error, the thermal effect of lead tetrachloride dissolution in carbon tetrachloride consists of + 706.7 ± 8.1 cal/ mole.

Because of the extremely low stability of lead tetrachloride, the authors did not carry out all of the measurements of thermal effects in formation of the more concentrated solutions. Even at relatively low concentrations with which the author dealt, some turbidity was noted in the solutions while taking the measurements.

SUMMARY

1. Heats of the following reactions under standard conditions have been measured:

$$\text{a)}\ PbCl_4\,(\text{liq.}) + I_2\,(\text{sol.}) \rightarrow PbCl_2\,(\text{cr.}) + 2ICl\,(\text{sol.}),$$

$$\text{b)}\ I_2\,(\text{sol.}) + Cl_2\,(\text{g.}) \rightarrow 2ICl\,(\text{sol.}).$$

The first reaction has been found to be exothermic and equal to −19793 ± 64 cal.; the second reaction has been found to be exothermic and equal to −6395 ± 6 cal.

2. From the data obtained, the heat of formation of lead tetrachloride from crystalline lead chloride and gaseous chlorine has been found. The effect of the reaction has been found to be endothermic, and equal to + 7003 ± 76 cal, i.e.,

$$PbCl_2\,(\text{cr.}) + Cl_2\,(\text{g.}) \rightarrow PbCl_4\,(\text{liq.}) + 7003 \pm 76\ \text{cal.}$$

3. From data obtained, and from literature data by calculation, it has been found that the standard heat of formation of $PbCl_4$ (liq.) from elementary substances is equal to 78.85 kcal/ mole, i.e.,

$$Pb\,(\text{cr.}) + 2Cl_2\,(\text{g}) \rightarrow PbCl_4\,(\text{liq.}) - 78.85\ \text{kcal/mole}$$

4. The thermal effect of lead tetrachloride dissolution in carbon tetrachloride has been measured under standard conditions. The thermal effect has been found to be endothermic, and equal to + 706.7 ± 8.1 cal.

The author expresses his deep appreciation to Professors A. A. Grinberg and to K. P. Mischenko for their kind assistance in the work.

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MOLECULAR COMPOUNDS OF ALUMINUM BROMIDE WITH NITROBENZENE IN ETHYLENE BROMIDE SOLVENT

E. Ya. Gorenbein

An investigation of highly concentrated electrolyte solutions has demonstrated that the law of decrease in molar electroconductivity corrected for viscosity with respect to dilution is followed by all highly-concentrated electrolyte solutions [1]. It has been demonstrated at the same time that the isotherms $\mu \cdot \eta - \varphi$ ($\mu \cdot \eta$ = product of molecular conductivity times viscosity, and φ equals dilution) are either superimposed upon one another, or are close together [2]. An investigation of the relationship between molar electroconductivity corrected for viscosity and dilution at various temperatures for a number of aluminum bromide complex compounds in nitrobenzene as the solvent have indicated that the isotherms $\mu_1 - \varphi$ (μ_1 equals molar electroconductivity corrected for viscosity) are not superimposed upon one another, but differ considerably among themselves [3]. This phenomenon is explained by the fact that instead of one, there are in fact two and more electrolytes in the solution, i.e., the system is not a binary one [4].

However, in calculating the molar electroconductivity, the author proceeded on the basis of one electrolyte dissolved, and the fact that new electrolytes may be formed as a result of interaction was not taken into account, for example,

$$KBr \cdot Al_2Br_6 + nC_6H_5NO_2 = KBr \cdot AlBr_3 + AlBr_3 \cdot nC_6H_5NO_2,$$

although both of these complexes conduct the current. Naturally, under such conditions electroconductivity isotherms would not be expected to superimpose upon one another.

Thus, on the basis of molecular electroconductivity isotherms, corrected for viscosity, it can be considered that one or more electrolytes are formed in the system.

Insofar as the molecular electroconductivity isotherms for complexes of aluminum halides with nitrobenzene do not superimpose, it can then be considered that the systems: $SbBr_3 \cdot AlBr_3 - C_6H_5NO_2$, $NaCl \cdot Al_2Br_6 - C_6H_5NO_2$, $NaBr \cdot Al_2Br_6 - C_6H_5NO_2$, $KBr \cdot Al_2Br_6 - C_6H_5NO_2$, $NH_4Br \cdot Al_2Br_6 - C_6H_5NO_2$ [3], are not binary, i.e., as a result of interaction of solvent with aluminum bromide, there are formed several electrolytes. Such assumption is justified by the fact that nitrobenzene forms several complex compounds with aluminum halides. Thus, for example, with nitrobenzene, aluminum chloride forms the compounds $AlCl_3 \cdot 2C_6H_5NO_2$, $AlCl_3 \cdot C_6H_5NO_2$ [5] and $Al_2Cl_6 \cdot C_6H_5NO_2$ [6]. Aluminum bromide produces with nitrobenzene two compounds, $AlBr_3 \cdot C_6H_5NO_2$ [7] and $AlBr_3 \cdot 2C_6H_5NO_2$ [8]. However, by the method of thermal analysis, only one compound, $AlBr_3 \cdot C_6H_5NO_2$ [7] was found. A compound of the same composition was determined by Klochko [9], who studied the electroconductivity, viscosity and specific gravity for the binary system $AlBr_3 - C_6H_5NO_2$ over the entire range of concentrations.

From $\mu_1 - \varphi$ isotherms for the systems consisting of $AlBr_3$ complexes with halides of the Groups I and V elements of the periodic system and nitrobenzene as the solvent, it follows that there should be more than one electrolyte in the solution, the author resolving therefore, to study the interaction of $AlBr_3$ with $C_6H_5NO_2$ in ethylene bromide as the solvent for two isomolar concentrations and at various temperatures. For this purpose the following properties were studied: viscosity, electroconductivity and specific gravity over the entire range of concentrations; the total moles of $AlBr_3 + C_6H_5NO_2$ remaining constant at all times per one mole of solvent ($C_2H_4Br_2$).

Speaking of a complete range of concentrations, the author had in mind those components whose interactions have been studied in the given case ($AlBr_3$ and $C_6H_5NO_2$).

Ethylene bromide in this system was considered as the medium, which made it possible to carry out the investigation at relatively low temperature, and to work with substances of limited solubility. This was justified by another fact that ethylene bromide does not form complexes with aluminum bromide [10]. Thus, investigations of such a type, it would seem, meet the demands of physico-chemical analytical principles.

TABLE 1

Mole ratio $\frac{AlBr_3 + C_6H_5NO_2}{C_2H_4Br_2} = 0.05$. Temperature 20°

$AlBr_3$ (mol. %)	d_4^t	$\eta \cdot 10^2$	$AlBr_3$ (mol. %)	d_4^t	$\eta \cdot 10^2$
100	2.2352	1.999	38.01	2.1631	1.985
71.81	2.1951	2.052	12.62	2.1380	1.878
62.56	2.1858	2.054	0	2.1248	1.819
50.05	2.1738	2.021			

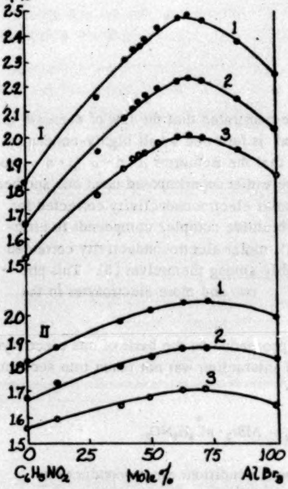


Fig. 1. Relation of viscosity isotherms for a ternary system to composition for two isomolar concentrations: I) 0.15 and II) 0.05. 1) 20°; 2) 25°; 3) 30°.

Starting Substances and Working Procedure

Nitrobenzene was purified according to Bruner [11], dried over fused calcium chloride, then distilled, dried over P_2O_5, and finally distilled into tapered test tubes, which were sealed immediately after filling. Samples distilling at one point were taken for the work. The aluminum bromide was prepared from aluminum shavings and bromine, and was kept in the same manner as described in preceding articles [2]. After thorough purification, the ethylene bromide was frozen out, dried over fused calcium chloride, distilled, dried a second time, and then distilled into test tubes which were sealed.

Electroconductivity was measured with a vacuum tube oscillator with optical indicator, diagram of which is shown in reference [12]. Measurements were taken to avoid traces of moisture in the work [13]. Thermostatic temperature was maintained with an accuracy of ± 0.1°.

Electroconductivity, Viscosity and Specific Gravities

$AlBr_3-C_6H_5NO_2$ has been investigated many times, but due to the limited solubility of $AlBr_3$ in $C_6H_5NO_2$ at room temperature, it was not possible to follow changes in any one property over a complete range of concentrations of components.

It was established during investigation of electroconductivity for the indicated system that with an increase in concentration of $AlBr_3$ the specific electroconductivity forms one maximum [14]. Investigation of the same system over the complete range of concentrations of components at a temperature of 100° made it possible to distinguish 2 maxima and 1 minimum, corresponding to an equimolecular composition of the compound. Other properties of this system which were studied pointed to the same composition for the complex [9].

The interaction of $AlBr_3$ with $C_6H_5NO_2$ was studied at two isomolar concentrations of 0.05 and 0.15 in ethylene bromide as solvent, carried out at 20°, 25° and 30°.

A study of the interaction between two components in an indifferent medium made it possible to observe a change of one or the other property within the entire range of concentrations because the 2 components were changing, and the third — the solvent — was constant; a study was carried out, starting with the binary system, for example A—B, and again with the ternary system, A—B—C, and again with the binary system B—C, with constant mole ratio of components.

To avoid overburdening the paper with extensive numerical data, only data for 20° are given. The remaining results of measurements are presented graphically in Figs. 1 and 2.

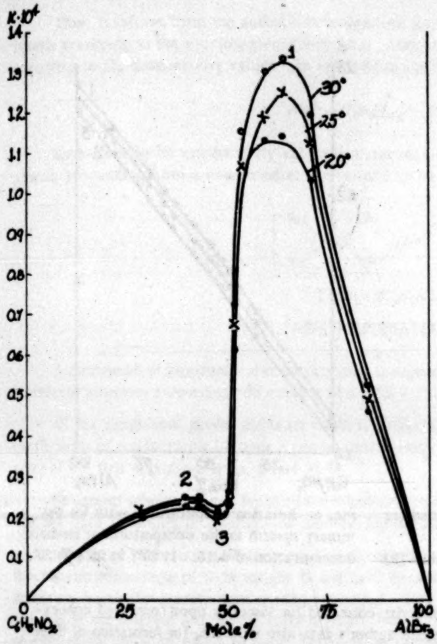


Fig. 2. Dependence of specific electroconductivity isotherms for a ternary system on composition at isomolar concentration of 0.15. 1) $Al_2Br_6 \cdot C_6H_5NO_2$; 2) $AlBr_3 \cdot 2C_6H_5NO_2$; 3) $AlBr_3 \cdot C_6H_5NO_2$.

TABLE 2

Temperature 20°

$\frac{AlBr_3+C_6H_5NO_2}{C_2H_4Br_2}$	$AlBr_3$ (mol. %)	$d_{4°}^{t}$	$\eta \cdot 10^2$	$\kappa \cdot 10^4$
0.1500	100	2.2835	2.248	—
0.1501	85.37	2.2494	2.384	0.453
0.1500	71.52	2.2142	2.462	1.028
0.1497	65.70	2.2020	2.484	1.134
0.1496	61.46	2.1926	2.470	1.121
0.1499	55.60	2.1770	2.451*	0.981
0.1496	53.50	2.1696	2.439	0.609
0.1498	51.78	2.1680*	2.424	0.219
0.1501	48.65	2.1585	2.391	0.189
0.1501	46.16	2.1520*	2.362	0.218
0.1596	44.04	2.1459	2.357	0.219
0.1499	40.47	2.1374	2.311	0.224
0.1499	29.73	2.1070	2.156	0.212
0.1504	0	2.0293	1.817	—

* Found by interpolation.

The relationship between viscosity of the system to ratio of $AlBr_3$ + $C_6H_5NO_2$ components, whose mole sum is taken as 100%, is presented in Fig. 1. The isotherms show results of measurement at two isomolar concentrations, 0.05 and 0.15.

It can be seen from the curves given that temperature increase and dilution lead to a decreased viscosity for the system, while the maximum gradually loses its depth.

Numerical values for viscosity plotted directly on the ordinates axis correspond to viscosity for the binary systems $AlBr_3-C_2H_4Br_2$ and $C_6H_5NO_2-C_2H_4Br_2$. The viscosity maximum resulting at these concentrations indicates formation in the solution of a compound having the composition $Al_2Br_6 \cdot C_6H_5NO_2$.

The curves in Fig. 2 indicate a relationship of specific electroconductivity to the concentration of components in the system for an isomolar concentration $AlBr_3$ + $C_6H_5NO_2$ equal to 0.15. With an increase in $AlBr_3$ concentration, the specific electroconductivity increases, then decreases a little, forming a gentle maximum, and on further increase in concentration increases sharply, passing through a maximum and falling quite rapidly. The character of the curves remains the same, i.e., both maximum and minimum are preserved upon introducing a correction for viscosity. Thus, from the isotherms of specific electroconductivity it can be postulated that three compounds are formed in the solution: $AlBr_3 \cdot 2C_6H_5NO_2$, $AlBr_3 \cdot C_6H_5NO_2$ and $Al_2Br_6 \cdot C_6H_5NO_2$; the latter compound is found to be more conductive. It is characteristic that the viscosity maximum coincides with the maximum for the specific electroconductivity corresponding to a composition of the complex with the highest electrical conductivity. With an increase in temperature, the electroconductivity increases somewhat, the product $\kappa \cdot \eta$ decreasing.

For a comparison of results obtained by the author for conductivity of the ternary system with the data obtained by Klochko [9] for the binary system $AlBr_3-C_6H_5NO_2$, the author has introduced a correction for viscosity Klochko's data for specific electroconductivity at 75° and at 100°. Results are given in Fig. 3.

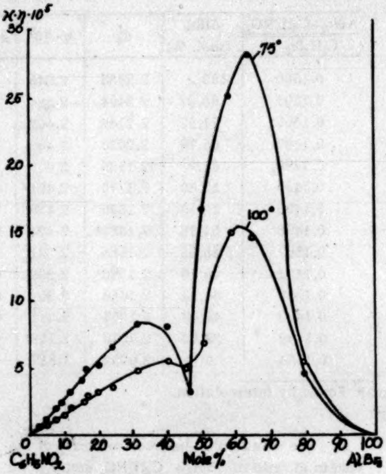


Fig. 3. Relationship of specific electroconductivity, corrected for viscosity of the $AlBr_3-C_6H_5NO_2$ binary system to composition at 75° and 100°, according to the data of Klochko [9].

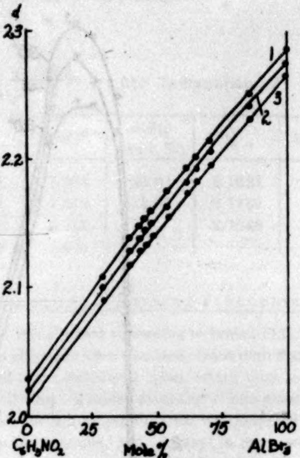


Fig. 4. Relation of specific gravity for the ternary system to the composition at isomolar concentration of 0.15. 1) 20°; 2) 25°; 3) 30°.

As can be seen from Fig. 3, the specific electroconductivity corrected for viscosity upon increased concentration of $AlBr_3$ forms two maxima and 1 minimum, which one author's data also indicate, for formation of three complex compounds, to which the author [9] paid no attention.

A certain shift of the minimum in the direction of lower $AlBr_3$ concentration is caused by difficulties in the experiment at the indicated temperatures for such compounds as $AlBr_3$ and $C_6H_5NO_2$.

The Fig. 4 isotherms characterize the relationship of specific gravity for the system to the ratio of components at isomolar concentration of $AlBr_3 + C_6H_5NO_2$ equal to 0.15. The bend on the isotherms, resulting from intersection of two straight lines, corresponds to compositions for the $AlBr_3 \cdot C_6H_5NO_2$ compound.

EVALUATION OF RESULTS

Analysis of the data obtained has indicated that, like $AlCl_3$, aluminum bromide with nitrobenzene forms 3 complex compounds which are apparently less stable, and therefore, were not characterized.

The fact that thermal analysis discloses only one compound is perhaps explained by the fact that the concentration region in which $Al_2Br_6 \cdot C_6H_5NO_2$ compound predominates possesses a higher viscosity, which inhibits crystallization. It is also known that nitrobenzene solutions possess the property of being considerably supercooled. In addition, the existence of explosions at high temperatures in the region of high $AlBr_3$ concentrations makes the experiment difficult.

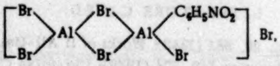
The procedure used by the author for a study of the interaction between two components in a third component, providing it is inert to the other two, , makes it possible to circumvent a number of difficulties which appear during the investigation of ternary systems (limited solubility under normal conditions, high temperature, decomposition of reactants, and others) and is in complete agreement with principles of physico-chemical analysis. A theoretical substantiation of this procedure is analyzed in detail by Izmai'lov [15].

It can be seen from the data given that for the systems in which two components form several compounds, the system's viscosity is primarily due to that compound which has the greatest viscosity in solution, and the best electrical conductivity. Moreover, during crystallizations of similar systems, it has been observed that the least dissociated and least electrical-conductive compound is the first to crystallize.

Thus, it follows from the author's investigations that aluminum bromide with nitrobenzene forms 3 compounds according to the electroconductivity data: $AlBr_3 \cdot 2C_6H_5NO_2$, $AlBr_3 \cdot C_6H_5NO_2$ and $Al_2Br_6 \cdot C_6H_5NO_2$, which, according to the conductivity values, are arranged in the following descending order:

$$Al_2Br_6 \cdot C_6H_5NO_2 > AlBr_3 \cdot 2C_6H_5NO_2 > AlBr_3 \cdot C_6H_5NO_2.$$

Such an order for conductivity values is in accord with possible structural schemes for these complex compounds, proceeding from a coordination number of four for aluminum:


(1)

$$[AlBr_2 \cdot 2C_6H_5NO_2]Br, \qquad (2)$$

$$[AlBr_2 \cdot 2C_6H_5NO_2]\,[AlBr_4]. \qquad (3)$$

A compound of equimolecular composition is expressed by the formula $Al_2Br_6 \cdot 2C_6H_5NO_2$, in which complex aluminum possesses a coordination number of 4 [16].

Of the compounds given, the least stable is $AlBr_3 \cdot 2C_6H_5NO_2$, which follows from the negative temperature coefficients of conductivity [9] over a concentration range with a predominance of this compound, and the character of the first maximum (Figs. 2 and 3).

Structural schemes given for aluminum bromide complex compounds with nitrobenzene are in full accord with the data according to transference numbers for the $AlBr_3-C_6H_5NO_2$ system.

Sheka and Pechenaya [17] have studied the transference numbers for the system $AlBr_3-C_6H_5NO_2$ within the concentration range of 2-28 weight % and have demonstrated that with increase in $AlBr_3$ concentration, the numerical values for transference numbers changed. This indicates without doubt that the system is not binary, and that in the solution are, as the authors point our, several complex ions. The change in concentration of $AlBr_3$ shifts the equilibrium between the complex compounds formed in solution and leads to predominance of one over the others, because of which a constancy in transference numbers cannot be observed.

The authors have demonstrated that during electrolysis the $AlBr_3$ concentration in the anode area increases and bromide ion concentration predominates, i.e., for a transference number equal to 0.73 for $\frac{1}{3}$ Al^{+++}, the corresponding transference number for bromide is 1.85, and for an aluminum transference number of 1.1, the bromide transference number is equal to 2.05. These data, it would seem, give grounds for assuming that in solution with $AlBr_4^-$ anion, there also exist free Br^- ions, which confirms the above-given structural schemes for the complex compounds forming during interaction of $AlBr_3$ with $C_6H_5NO_2$.

The results examined confirm without question the author's assumptions concerning the cause for the fact that isotherms of molecular electroconductivity corrected for viscosity for complex compounds of aluminum halides in nitrobenzene do not superimpose on one another, as was observed for other systems, which is apparently related to an interaction of nitrobenzene with aluminum halides.

Upon studying the system $AlBr_3-SbBr_3-C_6H_5NO_2$ by viscosity and electroconductivity, it has been demonstrated that the compound $AlBr_3 \cdot C_6H_5NO_2$ is more stable than the compound $SbBr_3 \cdot AlBr_3$ [18].

During dissolution of aluminum halide complexes of the type $MeHal \cdot Al_2Br_6$ in nitrobenzene, the latter apparently removes an aluminum bromide molecule from these compounds, with which it enters into reaction and forms new compounds. This also follows from the fact that alkali metal halides are not displaced by nitrobenzene from compounds with $AlBr_3$, since otherwise, because of their insolubility in $C_6H_5NO_2$, they would have precipitated out, which was not observed.

Thus, by a study of the isotherms of molecular electroconductivity corrected for viscosity, in solution for one or more electrolytes, a qualitative estimation can be made concerning the formation in solution of one or more electrolytes, because in this case the electroconductivity isotherms corrected for viscosity do not superimpose upon one another.

SUMMARY

1. Viscosity, electroconductivity and specific gravities for the system $AlBr_3-C_6H_5NO_2-C_2H_4Br_2$ with two isomolar concentrations, and at temperatures of 20°, 25° and 30° have been studied.

2. According to the electroconductivity data, $AlBr_3$ forms with $C_6H_5NO_2$ three compounds: $AlBr_3 \cdot 2C_6H_5NO_2$, $AlBr_3 \cdot C_6H_5NO_2$ and $Al_2Br_6 \cdot C_6H_5NO_2$. According to viscosity data, one compound, $Al_2Br_6 \cdot C_6H_5NO_2$, and according to specific gravity data $AlBr_3 \cdot C_6H_5NO_2$, are formed.

3. It has been demonstrated that the cause of the fact that electroconductivity isotherms, corrected for viscosity, for aluminum halide complexes in nitrobenzene do not superimpose on one another is due to interaction of components of the system with the formation of more than one electrolyte in solution.

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* T.p. = Consultants Bureau Translation pagination.

HETEROTRIACIDS

IV. SYNTHESIS AND ANALYSIS OF GERMANIUMTUNGSTOVANADIC ACID

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In synthesizing 1-vanadium-10-tungstogermanic acid, Ivanov-Emin [1] used germanium dioxide, ammonium paratungstate and ammonium vanadate. The ammonium vanadate used during synthesis was taken in larger amounts than would be required according to the stoichiometric calculations. The authors have not succeeded in reproducing the synthesis according to the above-indicated directions. In a majority of the cases, during acidification of a solution of the mixture of starting materials with 30% sulfuric acid to a definitely acid reaction, there precipitated out vanadium anhydride. Subsequent addition of acid in order to obtain the etherate caused formation of a yellow tungstic acid precipitate, and the etherate failed to separate. This fact is explainable, in all probability, by the fact that the authors attempted reproduction of the synthesis using considerably smaller quantities of starting materials. To carry out experiments with large amounts of starting material, however, was, to the authors, inexpedient, first because of the need to economize on germanium, and second, formation of tungsten acid precipitate would be unavoidable in any case.

Investigations completed by the authors on the synthesis of saturated germanium-molybdenumvanadic acid [2] have indicated that during the formation of the given heterotriacid, temperature control is a decisive factor, as well as the quantitative ratio of starting materials taken for the synthesis. It was natural to assume that these factors would have an effect during preparation of germaniumtungstovanadic acid, since heterotriacids containing tungsten are synthesized with greater difficulty than their molybdenum analogs [3]. On the other hand, during preparation of silico tungstovanadic acid by the etherate method, the authors established that the use of sodium paratungstate as starting material does not lead to production of the saturated heterotriacid. The problem in question is successfully solved if metatungstate is used for the synthesis [4].

Proceeding from the indicated concept, and from the fact that germanium is found to be like the silicon analog, the authors decided to develop a new method for synthesis of germaniumtungstovanadic acid. After a number of trials, the authors succeeded in solving this problem.

EXPERIMENTAL

Synthesis. Metallic germanium, normal sodium tungstate and sodium metavanadate were taken as the starting materials.

Metallic germanium was first converted to a solution by treating it with hydrogen peroxide, and by subsequent dissolution of the resulting germanium dioxide in alkali (NaOH). The normal sodium tungstate was converted into the metatungstate by addition of tungstic acid to a boiling solution of the sodium tungstate, weights taken of which were in the ratio of 1:1. A small amount of tungstic acid which did not react was filtered off [4].

Calculation of the amounts of substances necessary for synthesis of the heterotriacid was computed from the ratio of Ge:W:V as 1:10:2; however, four times as much vanadium was taken as required by stoichiometric calculation.

In separate experiments, the following amounts of materials were involved: Ge—0.05 g, $Na_2WO_4 \cdot 2H_2O$ — 2.3 g, WO_3 — 2.3 g, and $NaVO_3$ — 0.7 g.

Sodium germanate and vanadate solutions were added to a solution of the resulting sodium tungstate placed in a conical flask of 50 ml volume. The volume of liquid at the start of the experiment amounted to approximately 20-25 ml. The flask contents were acidified with several drops of H_2SO_4 (1:1), to the appearance of a bright orange color. 4-5 drops of the acid was used. The solution was boiled for 1.5 hours. During the boiling process, water was added several times in such a manner that the volume of liquid up to the completion of the experiment was kept equal to 10 ml. 5 ml of H_2SO_4 (1:1) was then added dropwise to the boiling solution, with vigorous stirring. At times, in some experiments, a slight turbidity resulted at the end of the sulfuric acid addition. The liquid was cooled, transferred to a separatory funnel of 50 ml volume, and ether added. Upon gentle shaking, drops of the orange etherate immediately began to form. Another 5 ml of H_2SO_4 (1:1) was added during the process of etherate separation. The solution over the etherate became yellow, and then green. The etherate was left undistrubed for 12-24 hours, then transferred to a low cylindrical vessel, the etherate decomposed with a small amount of water, and left to crystallize. The orange-red crystals which precipitated were filtered through a glass filter under vacuum. Yield of crystals amounted to 85% of theory.

Parallel experiments for preparation of germaniumtungstovanadic acid were arranged, in which twice as much vanadate was taken as required by stoichiometric calculation. In this case a mixture of acids apparently results. The determined amounts of tungsten and vanadium showed a W:V ratio of 10.4:1. Solutions of this acid began to show turbidity after 24 hours, while at the same time, solutions of the acid obtained as earlier were stable for a prolonged length of time.

Analysis. Water content of the heterotriacid obtained was determined by drying a sample (1 g) and roasting further to constant weight at a temperature of about 400°.

Preliminary decomposition of the heterotriacid by boiling with a mixture of sulfuric and phosphoric acids and water, as well as the subsequent determination of tungsten and vanadium, was carried out in a manner analogous to that described earlier in the analysis of silicotungstovanadic acid [4].

Considerable difficulty was encountered during determination of germanium. The generally accepted method for determination of germanium by distillation with hydrobromic acid led to negative results in all experiments carried out by the authors on analysis of a mixture of the germanium and tungsten compounds. No positive results were obtained by distillation with concentrated hydrochloric acid, either. This fact can be explained on the basis that the tungstic acid which precipitates holds tightly to the germanium, thus making complete distillation impossible. Introduction of oxalic acid into the analyzed mixture before distillation, to retain tungsten in solution, as well as to effect a preliminary reduction of the tungsten to lower valencies, increased the quantity of germanium distilled off, but the results were not reproducible. The amount of germanium distilled depended upon the rate of tungsten precipitation in proportion to the hydrochloric acid addition.

Brauer and Renner [5] recommend determination of germanium by tannin precipitation after a preliminary separation of tungsten in the form of tungstic acid. As the authors' experiments have demonstrated, with a low germanium content relative to tungsten, germanium in the filtrate does not precipitate with tannin. It is completely adsorbed and held fast by the tungstic acid precipitate.

After carrying out a series of experiments, the authors were able to establish that good results on determination of small quantities of germanium in the presence of considerable amounts of tungsten are obtained if the germanium is distilled off with concentrated hydrochloric acid in the presence of phosphoric acid and perhydrol, and the germanium precipitated from the distillate by means of tannin. The course of the analysis for germanium in germaniumtungstovanadic acid is given below.

Determination of germanium. A batch of the heterotriacid, 0.2-0.3 g was placed in the flask of a distilling apparatus [2] and dissolved in 3-5 ml of water. For retention of tungsten in the solution, with subsequent addition of the hydrochloric acid, 5 ml of H_3PO_4 (d 1.7) was added to the solution. Into the receiver with distillate was introduced 10 ml of HCl (1:1). The solution in the flask was heated, and 41 ml of concentrated HCl added gradually (as used) from a separatory funnel. Before introducing the last portions of hydrochloric acid, 1 ml of perhydrol was added. The hydrogen peroxide promotes the most complete distillation of germanium due to formation of small amounts of chlorine. After addition of all the hydrochloric acid, 20 ml of H_2SO_4 (1:1) was added, and the heating continued to separation of sulfuric acid fumes. 30-35 ml of concentrated ammonia and water was added to the hydrochloride solution from the receiver, transferred to a beaker, calculated so that the acidity remained equal to 0.5-1 N (total volume of solution 200-250 ml). After cooling, 20 ml of a 5% aqueous solution of tannin was introduced into the solution investigated, and the mixture left standing undisturbed up to 12 hours. The resulting light-brown precipitate was filtered off through a glass filter, washed and dried at 100-105° to constant weight. The ratio of germanium to tannin in the precipitate was equal to 1:30 [5]; hence, the coefficient, recalculated from the weight of precipitate of germanium content was equal to 0.0323. In Table 1 are given results of determination of germanium, tungsten and vandium recalculated to gram-atomic weights, and water content in moles (upon drying to constant weight at 105°).

TABLE 1

Results of Germaniumtungstovanadic Acid Analysis

Sample No.	Weight (g)	Ge		V		W		Ratio of Ge:V:W	H_2O	
		g	g-atom.	g	g-atom.	g	g-atom.		g	molecules
1	0.7839	0.0173	0.000238	0.0254	0.00050	0.4519	0.00245	1:2.1:10.2	0.0762	20
2	1.2023	0.0229	0.000315	0.0322	0.000631	0.6230	0.00338	1:2.0:10.7	0.1627	30
3	0.8025	0.0159	0.00021	0.0224	0.00044	0.4193	0.00228	1:2.1:10.7	0.0963	25

TABLE 2

Germanium, Tungsten and Vanadium Contents in the Precipitate After Reaction with o-Hydroxyquinoline

Found (in %)			Calculated (in %)		
Ge	W	V	Ge	W	V
3.30	91.00	4.85	3.65	91.30	5.05

The analytical results give grounds for believing that the given compound is related to the class of saturated heterotriacids, and may be represented by the formula $H_8[Ge(W_2O_7)_5V_2O_6]\cdot nH_2O$, where n = 20, 25, 30, on the basis of the Miolati-Rosenheim theory. In the authors' opinion, the amount of water of crystallization depends upon the conditions of crystallization and is not found to be constant. The total water content found by roasting at 400° amounted to 17-18.5%.

Saturated germanium tungstovanadic acid crystallizes readily in the form of orange-red crystals, and can be readily recrystallized from aqueous solutions. This compound is found to be relatively stable, both in solid form and in solutions. While the starting products(tungsten and vanadate) are precipitated by o-hydroxyquinoline only at very low acidity, the heterotriacid obtained is completely precipitated, even at acidities up to 1.3 N HCl.

After reaction with o-hydroxyquinoline, the precipitates were reanalyzed for their germanium, tungsten and vanadium contents. The average value of three determinations is given in Table 2.

Somewhat lower results were obtained for amounts of germanium, tungsten and vanadium, as compared with theory, which can be explained by experimental errors.

SUMMARY

1. A new, more effective procedure for synthesis of saturated germaniumtungstovanadic acid has been developed. Sodium metatungstate, and not ammonium paratungstate, was used as starting material.

2. Conditions for distillation of a small amount of germanium in the form of tetrachlorogermanium in the presence of large amounts of tungsten are specified.

3. It has been determined that precipitation of small amounts of germanium by means of tannin in the presence of large quantities of tungsten, after separation of the latter in the form of tungstic acid, does not produce positive results.

4. The composition of germaniumtungstovanadic acid which was synthesized has been determined, on the basis of which this compound can be represented by the formula $H_8[Ge(W_2O_7)_5V_2O_6]\cdot nH_2O$, where n equals 20, 25 and 30, and depends upon conditions of crystallization.

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* T.p. = Consultants Bureau Translation pagination.

DOUBLE DECOMPOSITION IN THE ABSENCE OF SOLVENT

II. THE QUATERNARY RECIPROCAL SYSTEM OF LITHIUM, POTASSIUM CHLORIDES, SULFATES AND TUNGSTATES

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

Internal Sections Through the Quaternary Reciprocal System, Li, K || Cl, SO_4, WO_4

Three sections through the composition prism described earlier in the literature [1] have confirmed the stability of complex compounds of $Li_2SO_4 \cdot K_2SO_4$, $Li_2WO_4 \cdot K_2WO_4$ and their extensive distribution within the quaternary reciprocal system Li, K || Cl, SO_4, WO_4. To establish dimensions for the inner crystallization volumes and their distribution, tetrahedrons for the prism, the compositions and locations of quaternary euctectic points for the system, and to study salt interactions found in the given system, five internal triangular sections through the prism-composition were studied by the visual-polythermal method [2].

EXPERIMENTAL

Stable Diagonal Section of $K_2Cl_2-Li_2WO_4-Li_2SO_4$

The lateral sides (Table 1, Fig. 1) are found to be stable diagonal sections of $Li_2WO_4-K_2Cl_2$ and $Li_2SO_4-K_2Cl_2$ of the corresponding reciprocal systems Li, K || Cl, WO_4 and Li, K || Cl, SO_4 [3]. $Li_2WO_4-K_2Cl_2$ is found to be a simple eutectic system with the eutectic at 532° and 44% K_2Cl_2, and a polymorphic conversion of lithium tungstate at 660° and 10.5% K_2Cl_2.

TABLE 1

Stable diagonal				Section	
$K_2Cl_2-Li_2SO_4$		$K_2Cl_2-Li_2WO_4$		$Li_2WO_4-Li_2SO_4$	
% K_2Cl_2	temperature	% K_2Cl_2	temperature	% Li_2SO_4	temperature
0	860°	0	738°	0	738°
5	672	5	698	5	730
10	590	10	664	10	720
15	538	15	648	20	702
25	490	25	618	30	680
30	460	30	592	35	666
32	456	35	572	37.5	660
35	486	40	550	40	656
40	520	42	540	45	648
52	584	45	544	50	636
60	619	50	560	60	614
72	668	60	612	65	600
80	700	70	660	68	596
90	740	80	698	70	614
100	774	90	740	80	690

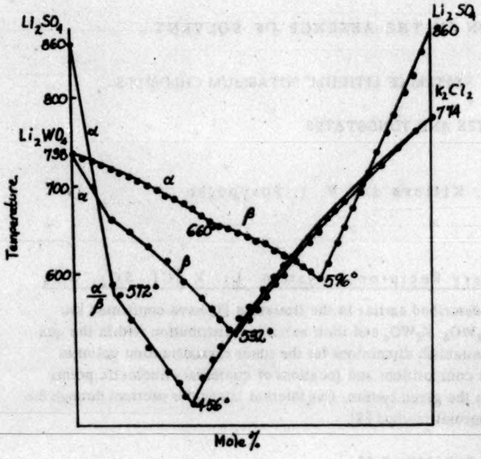

Fig. 1. Lateral sides of the $K_2Cl_2-Li_2WO_4-Li_2SO_4$ section.

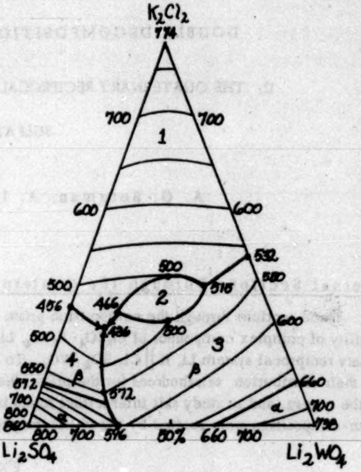

Fig. 2. $K_2Cl_2-Li_2WO_4-Li_2SO_4$. 1) K_2Cl_2; 2) $Li_2SO_4 \cdot K_2SO_4$; 3) β-Li_2WO_4; 4) β-Li_2SO_4.

The melting diagram for $Li_2SO_4-K_2Cl_2$ has a more complex character, consisting of three crystallization branches: α-Li_2SO_4, begining at 860° and 92.5% Li_2SO_4, β-Li_2SO_4 at 572° to the eutectic at 456° and 68% Li_2SO_4, and the K_2Cl_2 branch.

The third lateral side of the triangle for the $Li_2WO_4-Li_2SO_4$ profile is found to be the upper base side of the prism. It represents a eutectic system with eutectic at 596° and 68% Li_2SO_4. The Li_2WO_4 branch is complicated by the polymorphic conversion at 660° and 37.5% Li_2SO_4.

It was established by means of a number of sections through the triangular composition that the diagram for crystallization surface of $K_2Cl_2-Li_2WO_4-Li_2SO_4$ section consists of six fields of crystallization: α- and β-Li_2SO_4, K_2Cl_2, α- and β-Li_2WO_4, and $Li_2SO_4 \cdot K_2SO_4$ compounds (Fig. 2). The area of $Li_2SO_4 \cdot K_2SO_4$ binary salt separation, which contains K_2SO_4 as an exchange product, is outlined by the heavy line. This area on projection is in the form of a comparatively symmetrical lens, at one end of which is the 515° temperature, and at the other, 466°. This indicates that the crystallization volume for $Li_2SO_4 \cdot K_2SO_4$ complex lies beyond this stable section, but upon lowering of temperature, the complex reacting with lithium salts in liquid form decomposes, converting into a mixture of the three starting components. Consequently, appearance of the complex is found to be temporary, wedging out, and not participating in triangulation of the given triangular section. It can, therefore, be considered for practical purposes as a stable diagonal section for $K_2Cl_2-Li_2WO_4-Li_2SO_4$ with a triple eutectic point at 436° and 25% K_2Cl_2, 15% Li_2WO_4 and 60% Li_2SO_4.

Stable non-diagonal profile of $K_2Cl_2-(50\%\ Li_2WO_4 + 50\%\ K_2WO_4)-(50\%\ Li_2SO_4 + 50\%\ K_2SO_4)$.* Dissection proceeds from a cross section of the lateral reciprocal system, Li, K || SO_4, WO_4. Two lateral sides of the triangular composition are found to be stable non-diagonal sections of two squares for the reciprocal systems which are lateral facets of the prism-composition (Table 2, Fig. 3).

1) $K_2Cl_2-D_1$ is found to be the stable non-diagonal section of the reciprocal system, Li, K || Cl, WO_4, and bears the character of a simple eutectic system with eutectic at 514° and 16% K_2Cl_2;

2) $K_2Cl_2-D_2$, a stable non-diagonal cross-section of the reciprocal system, Li, K || Cl, WO_4, is found to be a eutectic system with eutectic at 585° and 31.5% K_2Cl_2;

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* Provisionary symbol: D_1 equals (50% Li_2WO_4 + 50% K_2WO_4); D_2 equals (50% Li_2SO_4 + 50% K_2SO_4).

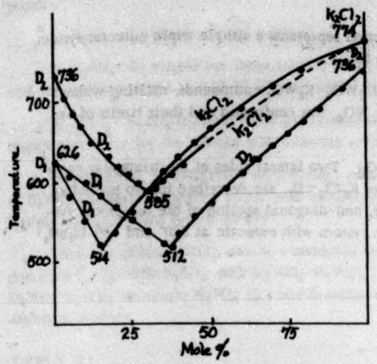

Fig. 3. Lateral sides of the $K_2Cl_2-D_1-D_2$ section.

TABLE 2

Stable non-diagonal				D_1-D_2 section	
$D_2-K_2Cl_2$		$D_1-K_2Cl_2$			
% K_2Cl_2	temperature	% K_2Cl_2	temperature	% D_2	temperature
0	734*	0	628*	0	628*
3	706	5	582	5	608
6	686	10	550	10	598
9	670	15	520	15	580
12	648	20	538	20	568
15	639	25	562	25	550
18	630	30	592	30	536
21	618	35	614	35	520
24	610	40	632	40	532
27	596	50	666	45	554
30	588	60	690	50	572
38	608	70	718	60	610
42	644	80	740	75	656

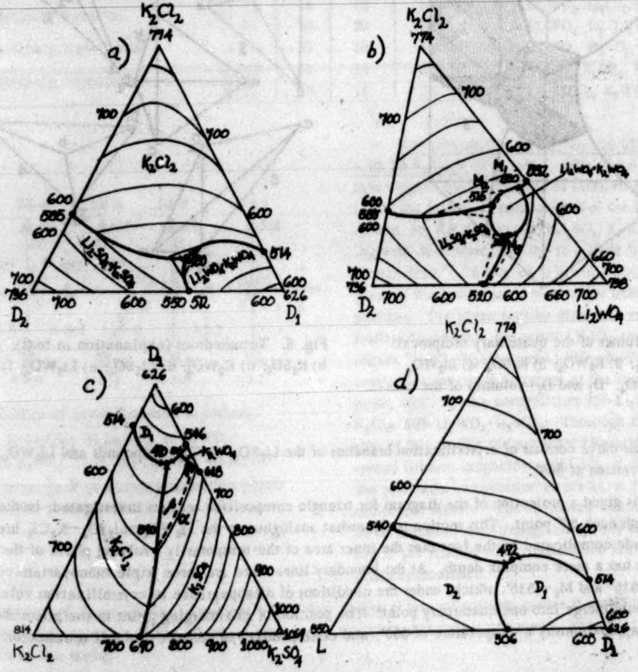
a)
K₂Cl₂
774
700
700
K₂Cl₂
600
585
600
600
Li₂SO₄-K₂SO₄
Li₂WO₄-K₂WO₄
514
600
626
700
736
D₂
700
600
550
512
600
D₁
b)
K₂Cl₂
774
700
700
600
M₁
M₂
Li₂WO₄-K₂WO₄
600
585
600
Li₂SO₄-K₂SO₄
660
700
700
736
D₂
700
600
520
600
660
700
Li₂WO₄
c)
D₁
626
514
600
D₁
K₂WO₄
600
700
K₂Cl₂
K₂SO₄
800
900
1000
814
K₂Cl₂
700
690
800
900
1000
K₂SO₄
d)
K₂Cl₂
774
700
700
600
540
492
D₂
D₁
514
600
626
550
L
506
600
D₁

Fig. 4. Sections through K, Li ‖ SO_4, Cl, WO_4 system. a) $K_2Cl_2-D_1-D_2$; b) $K_2Cl_2-Li_2WO_4-D_2$; c) $K_2Cl_2-D_1-K_2SO_4$; d) $K_2Cl_2-D_1-L$.

By a number of sections, the character of the crystallization surface for the given section (Fig. 4, a) was established. It consists of three crystallization fields: $Li_2SO_4 \cdot K_2SO_4$, $Li_2WO_4 \cdot K_2WO_4$ complex compounds, and K_2Cl_2.

In the Li, K ‖ Cl, SO_4, WO_4 quaternary system, the given section represents a simple triple eutectic system, with eutectic at 480° and a composition: 13% K_2Cl_2, 55% D_1, 32% D_2.

From the given section, the formation of $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$ compounds, melting without decomposition in the quaternary reciprocal system Li, K ‖ Cl, SO_4, WO_4, was confirmed and their limits of extension within the prism composition were established.

Additional section of $K_2Cl_2 - Li_2WO_4 - (50\%\ Li_2SO_4 + 50\%\ K_2SO_4)$. Two lateral sides of the triangular composition for the given section of $Li_2WO_4 - K_2Cl_2$ binary system and of $K_2Cl_2 - D_2$, are described in two preceding sections. The third lateral side, $Li_2WO_4 - D_2$ is found to be a stable, non-diagonal section of the reciprocal system Li, K ‖ SO_4, WO_4, and bears the character of a simple eutectic system with eutectic at 520° and 55% $Li_2SO_4 \cdot K_2SO_4$.

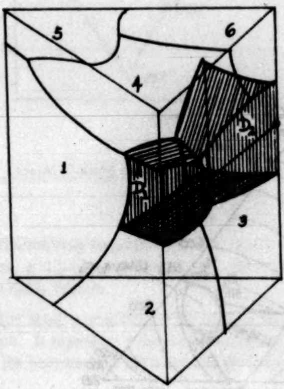

Fig. 5. Inner volumes of the quaternary reciprocal system. 1) K_2Cl_2; 2) K_2WO_4; 3) K_2SO_4; 4) Li_2WO_4; 5) Li_2Cl_2; 6) Li_2SO_4. D_1 and D_2) volumes of the complexes.

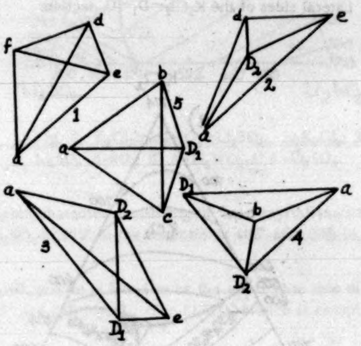

Fig. 6. Tetrahedrons (explanation in text). a) K_2Cl_2; b) K_2SO_4; c) K_2WO_4; d) Li_2SO_4; e) Li_2WO_4; f) Li_2Cl_2.

The liquidus curve consists of crystallization branches of the $Li_2SO_4 \cdot K_2SO_4$ compounds and Li_2WO_4, with polymorphic conversion at 660°.

In Fig. 4b is given a projection of the diagram for triangle composition section investigated; isotherms are plotted through each 50° point. This section is somewhat analogous to the $Li_2WO_4 - Li_2SO_4 - K_2Cl_2$ investigated earlier, but is made complicated by the fact that the inner area of the temporarily evolving phase of the $Li_2WO_4 \cdot K_2WO_4$ complex has a more complex depth. At the boundary lines there are three triple monovariant points: $M_1 - 530°$; $M_2 - 515°$ and $M_3 - 515°$, which, under the conditions of disappearance in crystallization volume of the complex, should merge into one quaternary point. The position of this merging point in the prism should be considered as at approximately a temperature of 500°, and corresponding in content to the II tetrahedron (see below).

The given section dissects the inside of the prism for the crystallization volume of Li_2WO_4 (α- and β-volumes), for K_2Cl_2, the volume of the compound $Li_2SO_4 \cdot K_2SO_4$, and the volume of the temporarily evolving phase of the $Li_2WO_4 \cdot K_2WO_4$ complex.

$K_2Cl_2-D_1-K_2SO_4$ section melting with decomposition. Two lateral sides of the triangular composition are found to be stable non-diagonal sections of two squares for the reciprocal systems, the lateral facets of the prism.

1) $K_2Cl_2-D_1$ was described earlier.

2) $K_2SO_4-D_1$ equals the inner section of Li, K ‖ SO_4, WO_4. The melting curve consists of three branches with intersecting points at 23% K_2SO_4 and 546°, and 33.5% K_2SO_4 and 618°.

3) $K_2Cl_2-K_2SO_4$ is found to be the lateral side of the lower base of the prismatic composition, and represents a eutectic for the system with eutectic at 690° and 42% K_2SO_4.

Results of the investigation on the inner sections are given in Fig. 4c. For such section, on the lateral sides of $D_1-K_2SO_4$, there appears a small area of K_2WO_4 separation, which wedges out rapidly within the system, and a triple eutectic point results at 490°.

Thus, the given section can be considered provisionally as stable, with a eutectic point at 490°, and composition: 12% K_2Cl_2, 20% K_2SO_4, 68% $Li_2WO_4 \cdot K_2WO_4$. The section dissects the volumes of crystallization: K_2Cl_2, $Li_2WO_4 \cdot K_2WO_4$ complex, K_2SO_4 (α- and β-volumes) within the prism, and the wedging out area of the K_2WO_4 exchange product.

TABLE 3

Tetrahedron	Character of the point	Composition (mole %)					Equilibrium phases
		$Li^{\cdot}$	$K^{\cdot}$	Cl'	SO_4''	WO_4''	
I	Quaternary eutectic	64	36	78	18	4	Li_2WO_4, Li_2Cl_2, K_2Cl_2, Li_2SO_4
II		80	20	20	64	16	Li_2WO_4, D_2, Li_2SO_4, K_2Cl_2
III	Quaternary transitional	73	27	18	43	39	Li_2WO_4, D_1, D_2, K_2Cl_2
IV	Quaternary eutectic	42	58	10	32	58	D_1, D_2, K_2SO_4, K_2Cl_2
V		27	73	16	12	72	D_1, K_2Cl_2, K_2WO_4, K_2SO_4

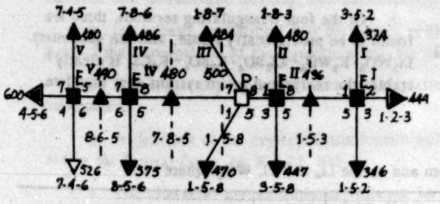

Fig. 7. Schemes of crystallization branching. 1) Li_2WO_4; 2) Li_2Cl_2; 3) Li_2SO_4; 4) K_2WO_4; 5) K_2Cl_2; 6) K_2SO_4; 7) D_1; 8) D_2. E — Eutectic point (quaternary); P quaternary transition point; I, II, III, IV, V — tetrahedrons.

Unstable section $K_2Cl_2-D_1$ (76.5% Li_2SO_4 + + 23.5% K_2SO_4)* (Fig. 4d). The given section was investigated for the purpose of clarifying expansion inside the prismatic composition of the Li, K ‖ Cl, SO_4 system, for the compound $2Li_2SO_4 \cdot K_2SO_4$ (2:1), melting with decomposition, the so-called lithium "langbeinite". In Fig. 4d is given a projection diagram of the investigated section for triangular composition. The given section dissects 3 volume crystallizations within the prism: K_2Cl_2 and two complexes, $Li_2SO_4 \cdot K_2SO_4$, and $Li_2WO_4 \cdot K_2WO_4$. The crystallization areas converge at the monovariant point, 492°, for the composition 21% Li_2WO_4, 24% K_2Cl_2, 55% $Li_2WO_4 \cdot K_2WO_4$. Thorough investigation of this profile did not show formation of widespread lithium langbeinite, $2Li_2SO_4 \cdot K_2SO_4$ within the prismatic composition of the Li, K ‖ Cl, SO_4, WO_4 reciprocal system. The indicated section was found to be unstable, non-triangulating, and non-participating in the scheme of crystallization branching for the prism composition.

Combination of three book sections and of four diagonal ternary sections makes it possible to obtain a clear idea about the structure of the prism, as well as the chemism between components, and about the indicated reaction shifts in the melts.

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* Provisionary symbol, L equals (76.5% Li_2SO_4 + 23.5% K_2SO_4).

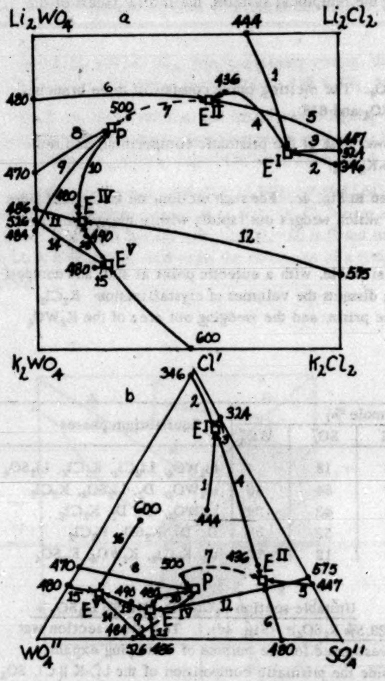

Fig. 8. Projection of crystallization branching on the lateral facet square of Li, K ‖ Cl, WO_4 and the base triangle, K ‖ Cl, SO_4, WO_4. Explanation in text and in Table 4.

The prismatic system Li, K ‖ Cl, SO_4, WO_4 composition diagram is divided into 8 principal crystallization volumes of salts (Fig. 5); two complexes $D_2-Li_2SO_4 \cdot K_2SO_4$ and $D_1-Li_2WO_4 \cdot K_2WO_4$ and six components Li_2Cl_2, Li_2SO_4, Li_2WO_4, K_2Cl_2, K_2SO_4, and K_2WO_4, where the lithium chloride, sulfate and tungstates are divided into sections with α- and β-modifications. The largest crystallization volume occurs with potassium chloride. The complex compound, $Li_2SO_4 \cdot K_2SO_4$, penetrates deeply into the system and occupies quite completely a large volume relative to the total pyramidal volume.

The volume of the $Li_2WO_4 \cdot K_2WO_4$ complex is much smaller and constitutes approximately $\frac{1}{2}$ of the sulfate complex volume.

The prism studied by four sections $Li_2WO_4-K_2Cl_2-Li_2SO_4$; $Li_2WO_4-Li_2SO_4 \cdot K_2SO_4-K_2Cl_2$; $Li_2WO_4 \cdot K_2WO_4-Li_2SO_4 \cdot K_2SO_4-K_2Cl_2$; and $Li_2WO_4 \cdot K_2WO_4-K_2SO_4-K_2Cl_2$ is divided into 5 tetrahedrons representing provisionary independent quaternary systems (Fig. 6).

I) tetrahedron $Li_2WO_4-K_2Cl_2-Li_2SO_4-Li_2Cl_2$;

II) $Li_2WO_4-D_2-K_2Cl_2-Li_2SO_4$;

III) $D_1-D_2-K_2Cl_2-Li_2WO_4$;

IV) $D_1-D_2-K_2Cl_2-K_2SO_4$;

V) $D_1-K_2Cl_2-K_2SO_4-K_2WO_4$.

Of the four triangulating sections, three are found to be provisionally stable, and the quaternary $Li_2WO_4 \cdot K_2WO_4-Li_2SO_4 \cdot K_2SO_4-K_2Cl_2$ is clearly stable; the reciprocal prism system can, therefore,

TABLE 4

Data on Orthogonal Projection of Li, K ‖ Cl, SO_4, WO_4 System and on the Li, K ‖ Cl, WO_4 Square*

No.	Temperature	System	% $Li^{\cdot}$	% $K^{\cdot}$	% Cl'	% WO_4''	Solid phases
1	444°	$Li_2WO_4-Li_2Cl_2-Li_2SO_4$	100	—	70	30	Li_2WO_4, Li_2Cl_2, Li_2SO_4
2	346	$Li_2WO_4-K_2Cl_2-Li_2Cl_2$	59	41	98	2	Li_2WO_4, K_2Cl_2, Li_2Cl_2
3	324	$Li_2SO_4-K_2Cl_2-Li_2Cl_2$	65	35	100	—	Li_2SO_4, K_2Cl_2, Li_2Cl_2
4	436	$Li_2WO_4-K_2Cl_2-Li_2SO_4$	82.5	17.5	62.5	37.5	Li_2WO_4, K_2Cl_2, Li_2SO_4
5	447	$Li_2SO_4-K_2Cl_2-D_2$	65	35	100	—	Li_2SO_4, K_2Cl_2, D_2
6	480	$Li_2WO_4-D_2-Li_2SO_4$	80	20	—	100	Li_2WO_4, D_2, Li_2SO_4
7	500	$Li_2WO_4-K_2Cl_2-D_2$	74	26	31	69	Li_2WO_4, K_2Cl_2, D_2
8	470	$Li_2WO_4-K_2Cl_2-D_1$	56.5	43.5	25	75	Li_2WO_4, K_2Cl_2, D_1
9	484	$Li_2WO_4-D_2-D_1$	38	62	—	100	Li_2WO_4, D_1, D_2
10	480	$D_1-D_2-K_2Cl_2$	43	57	14	86	D_1, D_2, K_2Cl_2
11	575	$D_1-K_2Cl_2-K_2SO_4$	24	76	100	—	D_1, D_2SO_4, K_2Cl_2
12	486	$D_1-D_2-K_2SO_4$	45	55	—	100	D_1, D_2, K_2SO_4
13	490	$D_1-K_2SO_4-K_2Cl_2$	36	64	16.5	83.5	D_1, K_2Cl_2, K_2SO_4
14	526	$D_1-K_2WO_4-K_2SO_4$	41	59	—	100	D_1, K_2WO_4, K_2SO_4
15	480	$D_1-K_2WO_4-K_2Cl_2$	26	74	19	81	D_1, K_2WO_4, K_2Cl_2
16	600	$K_2WO_4-K_2SO_4-K_2Cl_2$	—	100	50	50	K_2WO_4, K_2SO_4, K_2Cl_2

* Composition after recalculating for Cl' and WO_4'' ions is given in the Table.

be converted by these four sections into five tetrahedrons, of which not one, in the true sense, is a quaternary system, but rather is a quasi-quaternary system, since the volumes of the lateral complexes penetrate partially into the "foreign" tetrahedrons.

Each tetrahedron possesses one quaternary eutectic point and tetrahedron II – a transitional quaternary point. Their compositions are given in Table 3.

Schemes for the crystallization branching of the investigated quaternary reciprocal system are given in Fig. 7. On it are depicted triangulation planes (3, 4, 5, 6) and tetrahedrons formed by them (I, II, III, IV, V) as well as the triple eutectic and transitional points merging into the corresponding quaternary points. Projection of crystallization branching for the prism base K || Cl, SO_4, WO_4 (Fig. 8a) and the side facet Li, K || Cl, WO_4 (Fig. 8b) give a clear concept concerning distribution of the crystallization volumes of the salts, and the quaternary eutectic and transitional points. To construct the crystallization projection, the ionic composition for the triple eutectic points of the system was calculated, intersection points for the profiles through the prism with monovariant equilibrium curves given in Table 4.

Position of the quaternary points of the crystallization branching projections is provisionally found approximately. It can be made precise by plotting additional intersections on the prism; however, for solving the designated problem of disclosure of the general scheme for structure of the prism, the intersections completed in the prism were found sufficient.

As a general conclusion about the prism for the complex quaternary reciprocal system Li, K || Cl, SO_4, WO_4, it can be pointed out that 1) investigation and determination of the eight basic crystallization volumes for six components and two complexes has been demonstrated, and that both complexes, $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$ inside the quaternary system are stable; 2) for the Li, K SO_4, WO_4 system, there is a marginal non-diagonal system, the general character of which, on the whole, determines the character of the quaternary system, which is indicated by the simple eutectic character of the most interesting section $Li_2WO_4 \cdot K_2WO_4-Li_2SO_4 \cdot K_2SO_4-K_2Cl_2$.

SUMMARY

1. Five internal triangular sections through the composition prism have been studied, and it was established that $K_2Cl_2-Li_2WO_4-Li_2SO_4$ is a conditionally stable section with triple eutectic points at 436°; $K_2Cl_2-D_1-D_2$, definitely stable section with eutectic point at 480°; $K_2Cl_2-Li_2WO_4-D_2$ conditionally stable with transition point at about 500°; $K_2Cl_2-K_2SO_4-D_1$ provisionary stability, with eutectic point at 490°; $K_2Cl_2-D_1-L$ unstable, non-tetrahedron forming, non-participating in the formation of crystallization branching.

2. It has been established that the system is divided into 5 tetrahedrons by the four intersecting planes. In Table 3 the composition of the eutectic points for the tetrahedrons has been given.

3. The branching crystallization for the quaternary reciprocal system of Li, K || Cl, SO_4, WO_4 has been constructed.

4. Projections of the crystallization branching have been constructed for the prism base, K || Cl, SO_4, WO_4, and for the lateral facet, Li, K || Cl, WO_4.

5. The character and evolutionary scheme for the prism facets studied have been determined for the system Li, K || Cl, SO_4, WO_4.

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SOLUBILITY OF AMMONIUM METAVANADATE IN AQUEOUS AMMONIUM CHLORIDE SOLUTIONS

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The salting-out effect of ammonium chloride on ammonium metavanadate aqueous solutions is widely applied in practice of isolation and quantitative determination of vanadium, as well as during the preparation of ammonium metavanadate andits purification by recrystallization from ammonium chloride aqueous solution, or by washing with similar solutions. These processes are frequently mentioned in literature dealing with the subject; however, the data given are contradictory. Thus, according to some directions, separation of ammonium metavanadate should be carried out in boiling or hot solutions [1-5], and according to others, at 30-40° [6], while yet another recommendation is to salt it out in the cold [7, 8]. The ammonium chloride, according to a number of procedures, is introduced into the ammonium metavanadate solution in solid form, and according to others, in the form of saturated or concentrated aqueous solutions. Some recommend introduction of ammonium chloride into ammonium metavanadate solution up to the point of saturation [6, 8, 9], and use of an excess of the salting-out agent [7, 10, 11, 12], while others even consider 10-12% [13, 14], or even 0.9-1.3% ammonium chloride [13, 15] to be adequate. One opinion maintained is that ammonium chloride salts out ammonium metavanadate completely, while yet other works deny this [6, 12, 16]. A number of authors recommend washing the ammonium vanadate with concentrated or saturated aqueous ammonium chloride solution [5-7, 9, 12, 17-21], while others recommend for this purpose 2% [3, 15] and 1% [22] solutions.

In order to clarify this problem, an investigation of the solubility of ammonium metavanadate in aqueous ammonium chloride solutions was undertaken; for this purpose, the generally accepted method was used, consisting of a determination of solution concentrations while maintaining equilibrium by continuous stirring of the chemically-pure salts with distilled water in a water thermostat equipped with electrical heater and thermoregulator. The ammonium metavanadate in all experiments was introduced in such excess as to ensure its presence in the bottom phase, the quantity of ammonium chloride being varied at will. Investigation was carried out at 35° and at 60°. The solubility, in addition, was determined at room temperature (12.5 ± 2.0°). During analysis of the solutions and of the lower residues, the V content was determined colorimetrically with hydrogen peroxide in acid medium [18, 23], and Cl by titration with silver nitrate solution in the presence of nitric acid. Attainment of equilibrium was determined by coincidence in analytical data for two samples taken successively over a specified time interval. The quantities of V and Cl found were recalculated for NH_4VO_3 and NH_4Cl contents. Concentration calculation was carried out for 100 g of water and 100 g of solution. Resulting data are given in the table. Values for ammonium chloride solubility in water were taken from the literature data. Composition of the solid phase was determined by means of triangle solubility diagrams.

It can be seen from the table first of all that ammonium metavanadate solubility values, calculated for 100 g of water and for 100 g of solution, are almost identical. By means of triangle solubility diagrams, it was determined that at the indicated temperatures, neither crystalline hydrates nor double salts are formed in the system investigated.

Values obtained for solubility of ammonium metavanadate in water agree with the data of Zolotavin [26] and Meyer [2], and differ sharply (by 10-fold) from the values given in the reference manual of Lurye [27], which were found to be, as is not too difficult to determine, interpolated and 10-fold greater than the data of Meyer, differing as well from the data of Lachartre [28], regarding which an assumption has been voiced that they are 10-fold greater [29]. Pascal [30] gives corrected data on Lachartre. There is no doubt that Lurye and Lachartre have introduced an error, having incorrectly presented signs for solubility values, or having written 100 for the quantity of water in the directions instead of 1000. It is to be regretted that erroneously written data are being transcribed from one reference manual to another at present as well as previously.

The polythermic diagram constructed according to the table data is given in Fig. 1.

TABLE

Solubility of Ammonium Metavanadate in Aqueous Ammonium Chloride Solutions

No.	Temperature	Content in solution in g/100 g				Composition of moist bottom residue, wt. percent		Solid phase
		Water		Solution				
		NH_4VO_3	NH_4Cl	NH_4VO_3	NH_4Cl	NH_4VO_3	NH_4Cl	
1	12.5*± 2.0*	0.440	–	0.440	–	–	–	NH_4VO_3
2	12.5*± 2.0	0.085	0.262	0.085	0.261	–	–	–
3	12.5 ± 2.0	0.018	0.553	0.018	0.550	77.07	not found	NH_4VO_3
4	12.5 ± 2.0	not found	2.320	not found	2.270	–	–	–
5	13*	–	33.900	–	25.300	–	–	NH_4Cl
6	35*	1.150	–	1.140	–	–	–	NH_4VO_3
7	35	0.500	0.298	0.497	0.296	83.19	not found	NH_4VO_3
8	35	0.172	0.727	0.171	0.721	–	–	–
9	35	0.150	1.080	0.149	1.067	–	–	–
10	35	0.081	1.600	0.080	1.574	44.62	2.00	NH_4VO_3
11	35	0.027	2.610	0.026	2.540	30.44	1.84	NH_4VO_3
12	35	0.006	4.680	0.006	4.470	–	–	–
13	35	traces	9.870	traces	8.980	–	–	–
14	35	not found	12.920	not found	11.440	21.44	9.22	NH_4VO_3
15	35	not found	42.490	not found	29.820	20.13	76.65	NH_4VO_3 and NH_4Cl
16	35**	–	43.600	–	30.400	–	–	NH_4Cl
17	60*	2.550	–	2.490	–	–	–	NH_4VO_3
18	60	0.562	1.370	0.551	1.340	–	–	–
19	60	0.220	2.560	0.210	2.490	57.77	0.49	NH_4VO_3
20	60	traces	25.090	traces	20.060	–	–	–
21	60	not found	53.520	not found	34.860	–	–	–
22	60***	–	55.200	–	35.600	–	–	NH_4Cl

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* [24].

** [25].

*** [13].

Because of strong salting out of ammonium metavanadate with ammonium chloride, there is no crystallization area of the latter on the diagram.

The almost quantitative salting-out of ammonium metavanadate is readily attainable at various temperatures, and does occur, as the solubility data indicate, at the following concentrations in solution of ammonium chloride: at 12.5° about 1.5, at 35° about 10.0, and at 60° about 25.0 g per 100 g of water. These values presented in Fig. 2 show the limit for complete salting-out of ammonium metavanadate. In the same figure is given a section of the solubility curve for ammonium chloride in water.

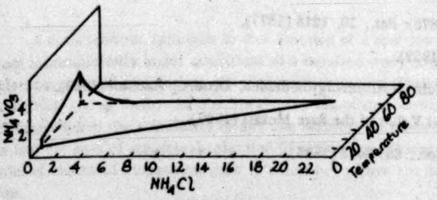

Fig. 1. Polythermal diagram of solubility (in g/100 g of the solution) in the $NH_4VO_3-NH_4Cl-H_2O$ system from 12.5 to 60°.

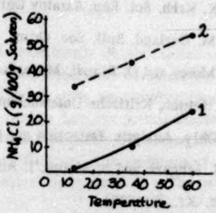

Fig. 2. Complete salting-out curves for ammonium metavanadate with ammonium chloride and solubilities of the latter in water. 1) Complete salting-out of NH_4VO_3 from aqueous solution; 2) NH_4Cl solubility in water.

It can be seen in Fig. 2 that complete salting-out of ammonium metavanadate occurs in solution not saturated with ammonium chloride. This attests to the impracticability of introducing excessive amounts of ammonium chloride, or of bringing the solutions up to saturation with ammonium chloride, as recommended by a number of authors, as well as the use of saturated versus concentrated solutions of ammonium chloride for washing the ammonium metavanadate.

As can be seen from the data given, with increased temperature ammonium chloride consumption increases during salting out. Thus, upon introducing solid ammonium chloride into ammonium metavanadate solution, there is required per 1 part by weight of the latter, for its complete isolation: at 12.5° 1.5:0.44 = 3.4, at 35° 10.0:1.15 = 8.7 and at 60° 25.0:2.55 = 9.4 parts by weight of NH_4Cl. Consumption of ammonium chloride is considerably decreased as the ammonium metavanadate precipitation is carried out from saturated solutions at increased temperatures, and the amount of ammonium chloride by calculating for complete salting out of ammonium metavanadate in the cold.

The minimal quantity of ammonium chloride required in this case should be calculated according to the equation $x = \frac{a \cdot \underline{b}}{100}$, where a is the quantity of ammonium chloride in weight percent of the quantity of water, determined by means of a salting-out curve for a specified cooling temperature of the solution; b is the quantity of water in the solution; and x is the quantity of ammonium chloride sought for. Thus, for example, given the case of an aqueous saturated solution of ammonium metavanadate at 60° which is then cooled to 12.5°, the ratio between minimum required amount of ammonium chloride and the quantity of ammonium metavanadate, will be equal to 1.5:2.55 = 0.6. Upon saturating ammonium metavanadate solution at higher temperature, and with a subsequent more extensive cooling (cooling to a lower temperature than before), the value for the ratio investigated is lowered even more.

Some authors recommend applying an aqueous solution of ammonium chloride instead of the solid, during the isolation of ammonium metavanadate. This is quite feasible under the conditions for ensuring proper concentration of ammonium chloride which is in direct relation to the value, b, in the equation quoted above.

An ammonium chloride concentration equal to 10-20% as recommended by some authors, is inexpedient, since it is only justifiable in those cases where salting out is carried out at 40°. A concentration of ammonium chloride equal to 1-2%, as recommended by other authors, is rational only when cooling below 12.5° is carried out.

SUMMARY

From data on combined solubility of ammonium metavanadate and ammonium chloride in water, the optimal conditions for separation and washing of ammonium metavanadate by the use of ammonium chloride can be determined.

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COMPOSITION OF THE SOLUBLE COMPLEX BETWEEN NICKEL COMPOUNDS AND DIMETHYLGLYOXIME FORMED IN THE PRESENCE OF OXIDANTS

L. S. Nadezhina and P. N. Kovalenko

A conscientious approach to the selection of a reaction suitable for colorimetric determination of any element is possible only under conditions of a detailed study of the basic physico-chemical characteristics for the colored compound in solution: its molar extinction coefficient, equilibrium constant, spectrophotometric characteristics, and so forth. An obscure conception of the chemism of the process does not permit theoretical substantiation of the suitability of any one reaction for quantitative determinations, and thus forces the investigator into the path of empirical selection of optimal conditions for each specific case. Compositions of a whole series of chemical compounds used in colorimetry have not been accurately characterized up to the present time.

Interaction of nickel salts with dimethylglyoxime, occurring in the presence of an oxidant, to form an intense orange-red colored compound is the basis of most colorimetric methods for determination of nickel. The chemism of the reaction, and the composition of the resulting compound, however, cannot be considered to have been accurately characterized. Numerous investigations of this reaction, carried out by various authors, have been directed chiefly to a study of the determination of nickel in various media and with various oxidants.

The composition of the nickel complex with dimethylglyoxime has been investigated by Feigl [1], who offered the hypothesis that the presence of an oxidant, Ni^{2+} ion converts into Ni^{4+}, the latter forming with dimethylglyoxime (H_2Dm) a brightly-colored compound corresponding to the formula $[Ni(HDm)_2O]$.

This statement remained unchallenged for a long time, and only recently have there appeared papers in the literature again devoted to this problem. Thus, in the work of Hurman [2], there is found indication that nickel in the presence of an oxidant forms two types of colored compounds — with two and four molecules of dimethylgyoxime, which do not separate from each other.. In subsequent works, Hurman's opinion did not find support, and so was not developed further. Babko has carried out extensive and systematic investigation of the chemistry of this reaction, using I_2 as the oxidant, and has proposed a theory that in course of reaction, the dimethylglyoxime, and not nickel, is oxidized, and that the colored compound formed during the reaction is found to be a complex ion of divalent nickel with unstable oxidation products of dimethylglyoxime [3]. In such case, formation of several kinds of complexes can be assumed. Experiments by Andreev and Azrelyan [4] did not confirm this assumption of Babko, but on the contrary, led the authors to a conclusion that nickel is oxidized in the reaction course. In contrast to Feigl, Andreev and Azrelyan consider that nickel goes to the trivalent, and not the tetravalent, state, entering as such into the composition of the complex. The work of Yatsimirsky [5] gives reason to believe that there may possibly exist two types of soluble nickel complexes with dimethylglyoxime (one with three, and one with a single molecule of H_2Dm, the latter complex being colorless).

From what has been indicated above, there are indications that the chemistry of formation of soluble nickel complexes with dimethylglyoxime cannot be considered yet as having been completely worked out; the authors, therefore, have studied the fundamental physico-chemical characteristics of this complex in the presence of various oxidants in order to define more closely data which are already available on the composition of the complex.

EXPERIMENTAL

Work was carried out on a photoelectric colorimeter, FEK-2, equipped with galvanometer, with a sensitivity of $5 \cdot 10^{-7}$ A/mm/m. Optical density of the solution (D) was determined by the differential method, using light filters whose characteristics were λ 500 mμ, λ 550 mμ, and λ 450 mμ. I_2, Br_2, $K_3[Fe(Cn)_6]$ and $(NH_4)_2S_2O_8$ were used as oxidants. Investigation of the effects of NH_4OH and of NaOH upon the D value indicated beforehand that the latter is not dependent upon their concentrations in the solution. In all subsequent experiments, therefore, the NaOH or NH_4OH concentration was kept equal to 0.5 M.

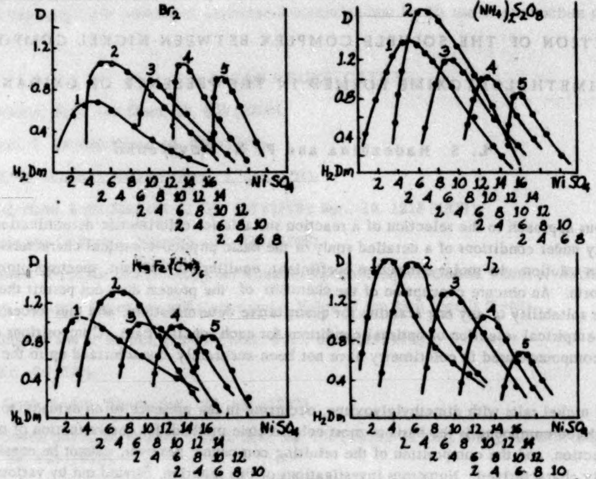

Fig. 1. $NiSO_4-H_2Dm-Ox$ system in ammoniacal medium. Composition is given in milliliters of 0.01 M solutions. Total volume of a mixture of the three components is 20 ml. Quantity of oxidant: 1) 4 ml; 2) 6 ml; 3) 8 ml; 4) 10 ml; 5) 12 ml.

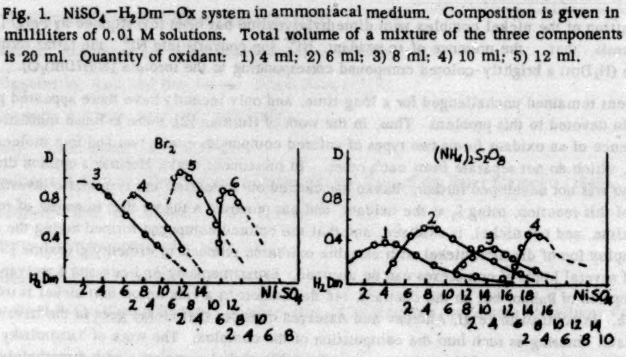

Fig. 2. $NiSO_4-H_2Dm-Ox$ system in alkaline medium. Composition is given in milliliters of 0.01 M solutions. The total volume of three-component mixture was 20 ml. The quantity of oxidant: 1) 2 ml; 2) 4 ml; 3) 6 ml; 4) 8 ml; 5) 10 ml; 6) 12 ml.

Physico-chemical analysis of the composition of nickel complexes with dimethylglyoxime in the presence of various oxidants. Using the physico-chemical analytical method developed by Babko [6] for the case of ternary systems, the authors investigated the following systems in alkaline and in ammoniacal media: $NiSO_4-H_2Dm-I_2$, $NiSO_4-H_2Dm-Br_2$, $NiSO_4-H_2Dm-K_3[Fe(CN)_6]$, $NiSO_4-H_2Dm-(NH_4)_2S_2O_8$, as well as the system $NiSO_4-H_2Dm$ in alkaline medium (in the latter case, oxygen of the air playing the role of oxidant). In a general way, composition of the investigated system can be expressed in the form of a tetrahedron whose peak is the solvent, water, and whose base is the triangle $NiSO_4-H_2Dm-Ox$ (where Ox. is the oxidant).

For a more complete characterization of the system, the authors studied four sections of the tetrahedron, parallel to the base, with concentrations for initially equimolar solutions, equal, respectively, to 0.006, 0.008, 0.010, 0.012 M. Investigation was carried out parallel to the $NiSO_4-H_2Dm$ side.

Optical density of the solution was measured at various sections of the spectrum, but in all cases the D maximum corresponded to the same composition; therefore, in Figs. 1-2, only data obtained from work with the green light filter (λ 500 mμ) are presented.

In some cases formation of nickel hydroxide of $Ni(HDm)_2$ was observed. These sections of the curves remain uninvestigated, and are shown by the dotted line in such cases where they could be extrapolated. In both alkaline and ammoniacal media, the extinction maximum of the solutions corresponded in almost all cases to a ratio of $NiSO_4 : H_2Dm = 1 : 3$ (Figs. 1 and 2).

The colored compound from nickel and dimethylglyoxime obtained in the absence of oxidant (Fig. 3) is in no way distinctive in its spectrophotometric characteristics from the analogous complexes obtained in the presence of I_2, Br_2, $K_3[Fe(CN)_6]$ and $(NH_4)_2S_2O_8$. However, the time required for establishment of maximum intensity in color for the first case is much longer and depends to a considerable extent upon the NaOH concentration of the solution. Thus, for example, maximum coloration in 0.1 N NaOH is observed after 2.5 hours, and in 1.0 N NaOH after only 30 minutes.

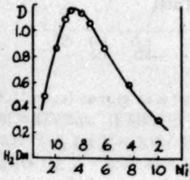

Fig. 3. $NiSO_4-H_2Dm$ system in 0.5 N NaOH. Oxidant: oxygen of the air. Composition given in milliliters of 0.01 M solutions. Total volume of two-component mixture was 12 ml.

For general characterization of the $NiSO_4-H_2Dm-Ox$ ternary system, the triangles were constructed, on which curves were plotted, connecting points with same color intensity (isochromes) and making it possible to estimate the composition of the soluble complex of nickel with dimethylglyoxime (Figs. 4 and 5). For visual convenience, straight lines were plotted in the triangles, corresponding to the sections $NiSO_4 \cdot 3H_2Dm-Ox$, $NiSO_4 \cdot 2H_2Dm-Ox$, $NiSO_4 \cdot 2Ox-H_2Dm$.

In all cases, the center of the isochromes was situated on a straight line, $NiSO_4 \cdot 3H_2Dm-Ox$. This made it possible to assume that Ni reacts with dimethylglyoxime in a ratio of 1 : 3, independently of the nature of the oxidant. The ratio of $NiSO_4 : Ox$, however, apparently depends upon the nature of the oxidant, and is not found to be a whole number, but fluctuates within the range of 1.5-2.5.

Because of this fact, the experimentally-obtained isochromic centers, in most cases, were not located on the $NiSO_4-2Ox-H_2Dm$ straight line.

Investigation of the complex composition according to the method of logarithmic limits. Apart from the physico-chemical analytical method, data on the ratio between reacting components can be obtained by using the method of logarithmic limits. The latter is based upon utilization of a directly proportional function between the logarithm of the concentration of complex-forming materials and the logarithm of the solution's optical density. Upon plotting these values on a coordinate axis, a straight line results, the tangent of which corresponds to the number of H_2Dm groups bound with nickel.

The authors' investigations were carried out with nickel sulfate solution of concentration equal to $2.07 \cdot 10^{-4}$ M. Dimethylglyoxime was varied in the concentration range $0.08 \cdot 10^{-3}-10 \cdot 10^{-3}$ M. Concentration of oxidant was maintained constant in all cases and was equal to $2.0 \cdot 10^{-3}$ M. Measurements were carried out with different light filters, and in all cases analogous data were obtained.

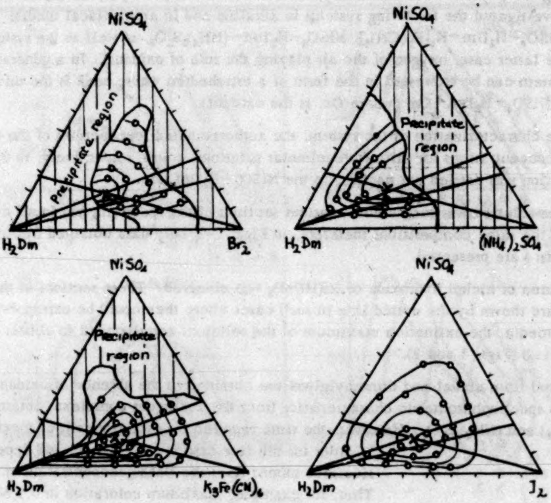

Fig. 4. Isochrome triangles for $NiSO_4-H_2Dm-Ox$ system in alkaline medium. Concentration of initial solutions of $NiSO_4$, H_2Dm and Ox was 0.1 M. Total volume of three-component mixture was 30 ml.

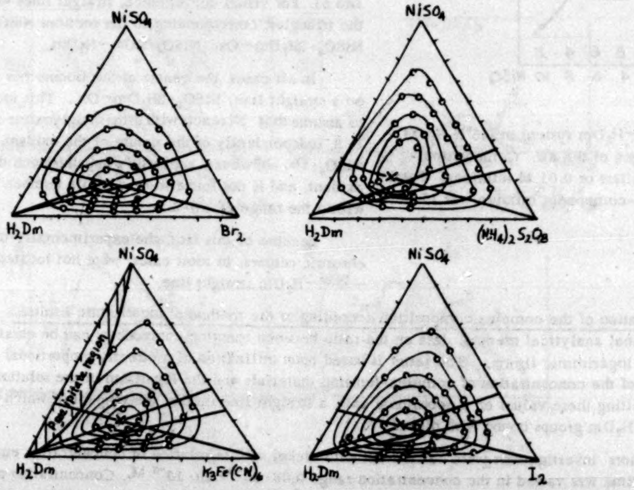

Fig. 5. Isochrome triangles for the system $NiSO_4-H_2Dm-Ox$ in ammoniacal medium. Concentration of initial solutions of $NiSO_4$, H_2Dm and Ox was 0.01 M. Total volume of three-component mixture was 20 ml.

In the table and in Fig. 6 results obtained from work with the green filter (λ 550 mμ) are given.

Data on the relationship between optical density of the solution to concentration of dimethylglyoxime obtained during work with different oxidants indicate that the type of oxidant does not affect the character of the reaction between nickel and dimethylglyoxime to any great extent. It became evident during a plot of the logarithimic graph (Fig. 6) that in both alkaline and ammoniacal media the n value, which characterizes the number of H_2Dm molecules entering into the complex composition, is close to three, which completely substantiates the data obtained by the method of physico-chemical analysis.

The section cut by a straight line on the abscissa axis at the equilibrium H_2Dm concentration equal to 1.0 M is directly related to the value for the equilibrium constant (K_e). This constant was calculated by Yatsimirsky [5] during the investigation of the reaction between nickel and dimethylglyoxime in the absence of oxidant and with prolonged standing of the ammoniacal solution (the role of oxidant being fulfilled by oxygen of the air) and was found equal to 10^{14}. The authors' data ($K_e = 1.4 \cdot 10^{12}$) are in sufficiently good agreement with the results of Yatsimirsky's calculations, and indicate that in all cases where formation of a soluble colored nickel complex takes place the nature of the oxidant affects only the process rate, and not its chemism.

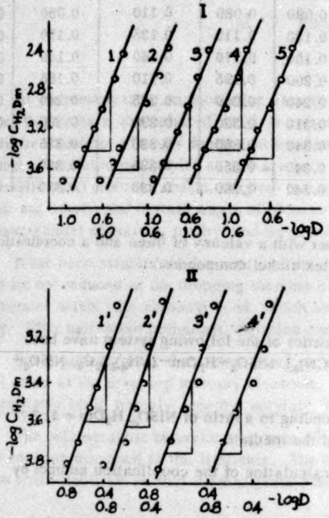

Fig. 6. Optical density as a function of the H_2Dm concentration in solution. I) Alkaline medium; II) ammoniacal medium. 1) I_2 (tg ∠ = 3.0); 2) Br_2 (tg ∠ = 2.6); 3) $(NH_4)_2S_2O_8$ (tg ∠ = 2.9); 4) $K_3Fe(CN)_6$ (tg ∠ = 2.7); 5) O_2 (tg ∠ = 2.9); 1') I_2 (tg ∠ = 3.1); 2') Br_2 (tg ∠ = 3.3); 3') $K_3Fe(CN)_6$ (tg ∠ = 2.9); 4') $(NH_4)_2S_2O_8$ (tg ∠ = 2.7).

EVALUATION OF RESULTS

The results obtained lead one to think that despite Babko's opinion [3], the oxidant does react with nickel but not with dimethylglyoxime, since, in such a reaction, stoichiometric ratios between the volumes of equimolar solutions of H_2Dm and oxidant would have been expected. Inasmuch as the hypothesis concerning unstable oxidation products of dimethylglyoxime capable of reacting with Ni^{2+} ions is concerned, which was not confirmed by a number of other authors, it is quite reasonable to assume, as has already been expressed by Andreev and Azrelyan [4], that in the course of reaction oxidation of Ni^{2+} to Ni^{3+} occurs, and that the latter then forms the soluble, bright-colored complex with three molecules of dimethylglyoxime.

The oxidation process $Ni^{2+} \rightleftharpoons Ni^{3+}$ has been found to be readily reversible, and depends upon the nature of the oxidant; the ratio of $NiSO_4$: Ox, therefore, does not remain constant. In the given case, the K_e for the reaction is sufficiently large to ensure an equilibrium shift to the side of the oxidized form, under conditions of negligible nickel concentration in the solution. With considerable $NiSO_4$ concentration (of the order of $1 \cdot 10^{-3}$M and greater) the soluble complex fails to form, even in the presence of excess oxidant, and the usual precipitate, $Ni(HDm)_2$, results. On the other hand, in the presence of large amounts of oxidant (0.1-1.0 M) there is observed decoloration of the solution, which is connected with oxidation of the dimethylglyoxime, since the addition of new H_2Dm to the solution renews the color.

Trivalent nickel compounds are not very numerous, but they do exist and are of sufficient stability. Ni_2O_3 is widely used in qualitative analysis. Hofman describes the Ni^{3+} complex with formoxime prepared by him, corresponding to the formula $Na_3[Ni(CH_2NO)_6]$ [1]; other specifications are available, indicating the possibility of compound formation in which nickel has a valency equal to 3. Moreover, by analogy with cobalt, which in almost all complexes is trivalent, Ni^{3+} should also give complexes whose K_e's are sufficiently great, thus ensuring shift of equilibrium to the side of formation of the oxidized form. The composition of the complex can then be represented by the formula $Ni(HDm)_3$.

TABLE

No.	Concentra- $H_2Dm\cdot 10^3$ M	D (ammoniacal medium)				D (alkaline medium)				
		I_2	Br_2	$(NH_4)_2S_2O_8$	$K_3Fe(CN)_6$	I_2	Br_2	$(NH_4)_2S_2O_8$	$K_3Fe(CN)_6$	O_2
1	0.08	0.070	0.080	—	0.070	—	—	—	—	—
2	0.10	0.120	0.140	0.070	0.120	—	—	—	—	—
3	0.16	0.160	0.160	0.120	0.190	0.050	0.050	0.045	0.030	0.040
4	0.20	0.200	0.210	0.180	0.220	0.090	0.080	0.110	0.050	0.085
5	0.30	0.220	0.230	0.230	0.250	0.130	0.115	0.135	0.120	0.110
6	0.40	0.240	0.250	0.255	0.280	0.160	0.170	0.160	0.140	0.165
7	0.60	0.255	0.265	0.280	0.290	0.200	0.195	0.210	0.185	0.190
8	1.00	0.270	0.280	0.295	0.300	0.240	0.240	0.255	0.240	0.260
9	2.00	0.315	0.320	0.310	0.310	0.310	0.320	0.290	0.300	0.320
10	4.00	0.330	0.345	0.320	0.330	0.340	0.360	0.330	0.335	0.345
11	8.00	0.335	0.350	0.315	0.330	0.340	0.355	0.335	0.330	0.340
12	10.00	0.330	0.350	0.320	0.330	0.340	0.360	0.330	0.330	0.340

In a similar treatment, nickel plays the role of a complex former with a valency of three and a coordination number equal to six, which is characteristic for the majority of complex nickel compounds.

SUMMARY

1. Using a physico-chemical method of analysis, the characteristics of the following system have been studied: $NiSO_4-H_2Dm-I_2$, $NiSO_4-H_2Dm-Br_2$, $NiSO_4-H_2Dm-K_3[Fe(CN)_6]$, $NiSO_4-H_2Dm-(NH_4)_2S_2O_8$, $NiSO_4-H_2Dm-$oxygen of the air.

2. It has been demonstrated that a complex is formed, corresponding to a ratio of $NiSO_4:H_2Dm = 1:3$, which is independent of the nature of the oxidant and the character of the medium.

3. Physico-chemical analytical data have been confirmed by calculation of the coordination number by the method of logarithmic limits.

4. A hypothesis has been advanced concerning the character of the interaction course with dimethylglyoxime in the presence of an oxidant.

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[4] A. S. Andreev, O. P. Azrelyan, J. Anal. Chem., 6, 375 (1951).

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* T.p. = Consultants Bureau Translation pagination.

POLAROGRAPHIC REDUCTION OF ETHERS

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At the present time an increasing variety of organic substances are under polarographic investigation, among them ethers, the value of which is presently very prominent in the development of organic synthesis. There are a number of works dealing with polarographic determination of ethers [1-5]. Among these works, a number of saturated carboxylic acids have been polarographed, namely: the ethyl esters of mono- and of dicarboxylic acids (formic, acetic, butyric, isobutyric, valeric, caproic, capronic, caprylic, malonic, succinic, adipic and others) and certain esters of chloroacetic acids. Such esters with conjugated double bonds as dimethyl oxalate, dibutyl phthalate, methyl and butyl methacrylate, as well as the sulfonic acid esters, were polarographed.

It has been established that esters of the saturated mono- and dicarboxylic acids without the conjugated bond are not reduced at the dropping mercury electrode up to 2.2 V. Esters of chloroacetic acid and the above-enumerated esters with carbonyl bond, which are conjugated with the ethylenic bond, are reduced polarographically. Their half-wave potentials, diffusion current constants, and diffusion coefficients, have been determined.

In the present work, the authors have set up the task of determining the behavior of a series of simple vinyl ethers at the dropping mercury electrode, as well as some esters with the carbonyl bond, conjugated with the ethylenic bond, namely: methyl acrylate, methyl and butyl methacrylates and free methacrylic acid.

The polarographic behavior of simple vinyl ethers, as well as methyl acrylate and free methacrylic acid, have not been discussed in the literature. The half-wave potentials and diffusion current constants, and the diffusion coefficients for methyl methacrylate published in the literature differ among themselves noticeably.

EXPERIMENTAL

Objectives of the Work and Methods of Measurements

All vinyl ethers in Table 1, synthesized according to the Favorsky-Shostakovsky method [6], were supplied by M. F. Shostakovsky. The other ethers used were prepared by distillation of the technical products. The characteristics of the ethers investigated and methacrylic acid are given in Table 1.

Polarography was carried out with a Gorky polarograph M-7, with a mirror galvanometer of Banner Factory manufacture, with a sensitivity equal to 200 mm/μA at a scale distance of galvanometer from mirror of 100 cm. Shunts from $1/5$ to $1/50$ sensitivity were used in the work.

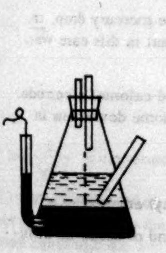


Fig. 1. Electrolyzer.

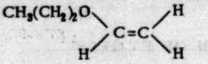
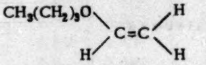
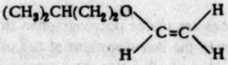
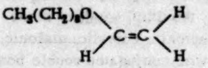
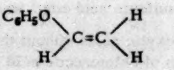
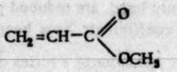
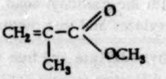
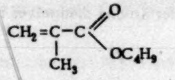
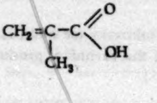
The vessel pictured in Fig. 1 was used for the electrolyzer. At the left is placed the current outlet from the anode, and at the right a tube for supplying nitrogen in order to remove oxygen from solution which is dissolved. Resistance of the electrolyzer for the solutions studied amounted to 3000 ohms.

Characteristics of the capillary during polarography of the vinyl ether was as follows: mass of the mercury drop, $\underline{m}$ = 1.75 mg; dropping period, t = 3.25 sec. Without a polarization voltage, the capillary constant was $m^{2/3} \cdot t^{1/6} = 1.507$ $mg^{2/3}\ sec^{-1/2}$.

The base electrolyte in the case of vinyl ethers was $(CH_3)_4NI$ ($\underline{c}$ = 0.25 mol/l in 75% C_2H_5OH) solution, as well as weak solutions of alkali and of acids. The vinyl ethers were polarographed in the concentration range from 1 to 15 mmol/l.

Esters with a carbonyl bond conjugated with an ethylenic bond were polarographed in the concentration range from 5 to 50 mmol/l; as the background electrolyte in this case, a more dilute solution $(CH_3)_4NI$ ($\underline{c}$ = 0.1 mol/l in 50% C_2H_5OH) was used.

TABLE 1

Name of compound and its formula	Boiling point	n_D^{20}
Vinylpropyl ether 	64-66°	1.3950
Vinylbutyl ether 	94	1.4026
Vinylisoamyl ether 	110-112	1.4065
Vinylnonyl ether 	205	1.4320
Vinylphenyl ether 	–	1.5220
Methyl acrylate 	80-83	1.403
Methyl methacrylate 	100	1.4158
Butyl methacrylate 	–	1.4228
Methacrylic acid 	161° (68.5° at 14 mm)	1.4310

For polarographing the esters, a capillary was used for which at 2.13 V the mass of the mercury drop, m, was equal to 0.64 mg, and the dropping period, t, was equal to 3.1 sec; the capillary constant in this case was, thus: $m^{2/3} \cdot t^{1/6} = 0.956$ mg$^{2/3}$ sec$^{-1/2}$.

All values of half-wave potentials ($E_{1/2}$) found refer to the potential toward a saturated calomel electrode. The anode potential relative to the saturated calomel electrode was equal to 0.33 V, with some deviations in the case of individual esters.

Vinyl Ethers

Polarographed were: vinylpropyl, vinylbutyl, vinylisoamyl, vinylnonyl and vinylphenyl ethers.

Using $(CH_3)_4NI$ as the background electrolyte, as well as dilute solutions of alkalies and of acids, no diffusion waves were obtained for the enumerated vinyl ethers in Table 1.

Esters with Conjugated Double Bonds

Diffusion waves were obtained for methyl acrylate, free methacrylic acid, methyl and butyl methacrylates, using $(CH_3)_4NI$ as the background solution. During the transition from lower to higher concentrations, there appeared maxima in the range from 1.8 to 2.2 V on the polarograms.

The maxima were suppressed by gelatin solutions for the concentration range from 0.0075 to 0.0275 (relative to the overall volume of solution investigated). Comparing the polarograms without gelatin with polaro-

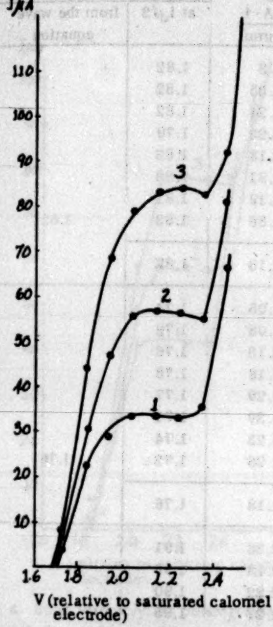


Fig. 2. Methyl acrylate polarograms. 1) c = 15 mmol/l; 2) c = 30 mmol/l; 3) c = 45 mmol/l. Background electrolyte $(CH_3)_4NI$ (c = 0.1 M in 50% C_2H_5OH).

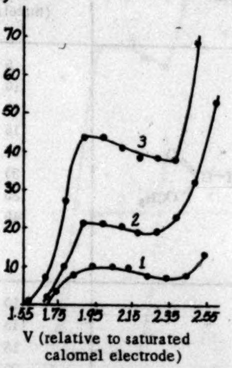


Fig. 3. Methacrylic acid polarograms. 1) c = 10 mmol/l; 2) c = 15 mmol/l; 3) c = 30 mmol/l. Background electrolyte $(CH_3)_4NI$ (c = 0.1 M in 50% C_2H_5OH).

grams in which gelatin was used, the authors came to the conclusion that by addition of gelatin they could bring the effect of the velocity of tangential movement of the mercury drop in the solution layer at the electrode to approximately zero.

The polarographic data obtained are given in Table 2 and in Figs. 2-7. It follows from their examination that the diffusion current values are in direct relation to the increase in concentration of ether.

The $E_{1/2}$ values were found from the polarogram by graphical means at $i_d/2$, as well as being obtained from the equation for polarographic wave

$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i},$$

if log $\frac{i}{i_d - i}$ is expressed graphically as a function of E at the value log $\frac{i}{i_d - i} = 0$.

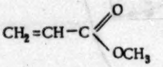
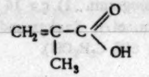
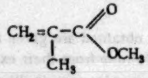
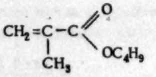
The number of electrons, n, participating in the electrode process is determined as the product of the gradient angle tangent to the resulting straight line on RT/F. The value, n, in the case of methylmethacrylate was found equal to 0.43, and for the methacrylic acid, 0.58, methyl methacrylate being 0.73, and butyl methacrylate 0.70.

Since the n values found are fractional numbers, then for the given case, n, there is found to be an apparent consumption of electrons. The theoretically expected n value for the specific processes in the case of reversibility is equal to 2. Thus it can be considered that the reduction processes for the enumerated ethers at the dropping mercury electrode are irreversible.

In addition, the n value was determined according to the Ilkovich equation $I = 605 \cdot m^{2/3} \cdot t^{1/6} \cdot D^{1/2} \cdot n \cdot c$. The diffusion coefficients for the polarographed ethers were calculated approximately, beforehand, according to

TABLE 2

Polarographic Data

Formula	Concentration, c (mmol/l)	Diffusion current, i_d (μA)	i_d/c $\frac{\mu A \cdot l}{mmol}$	Half-wave potential	
				at $i_d/2$	from the wave equation
	5	11.5	2.3	1.82	
	10	23.5	2.35	1.82	
	15	33.6	2.24	1.82	
	15	33.5	2.23	1.79	
	25	54.5	2.18	1.83	
	30	57.5	1.91	1.83	
	35	76.5	2.19	1.81	
	45	84.5	1.88	1.83	1.82
		Average	2.16	1.82	
	10	10.5	1.05	1.74	
	15	16.5	1.08	1.79	
	15	17.0	1.13	1.76	
	20	23.7	1.18	1.78	
	25	30.0	1.20	1.77	
	30	39.0	1.30	1.71	
	30	37.0	1.23	1.74	
	40	50.5	1.26	1.72	1.76
		Average	1.18	1.76	
	10	23.6	2.36	1.91	
	15	36.5	2.43	1.90	
	20	44.5	2.22	1.90	
	30	68.0	2.27	1.95	
	40	86.5	2.16	1.92	
	45	102.0	2.27	1.88	1.90
		Average	2.28	1.91	
	10	20.5	2.05	1.91	
	15	30.2	2.01	1.90	
	20	41.0	2.05	1.92	
	20	43.0	2.15	1.92	
	25	52.5	2.10	1.93	
	30	58.0	1.95	1.91	
	40	83.0	2.07	1.93	
	40	78.0	1.95	1.94	
	45	90.0	2.00	1.93	1.925
		Average	2.03	1.92	

the formula composed on the basis of the Stokes-Einstein equation for spherical molecules at infinite dilution in aqueous solutions:

$$D = \frac{3.32 \cdot 10^{-5}}{(V_m)^{1/3}} \text{ cm}^2 \text{ sec}^{-1},$$

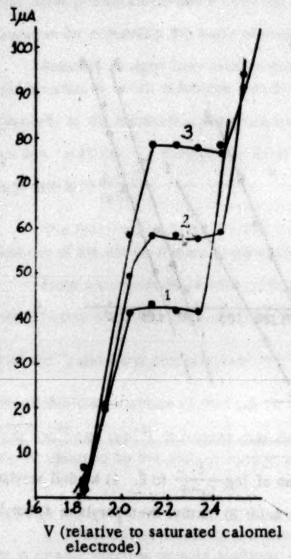


Fig. 4. Butyl methacrylate polarograms. 1) c = 20 mmol/l; 2) c = 30 mmol/l; 3) c = 40 mmol/l. Background electrolyte $(CH_3)_4NI$ (c = 0.1 m in 50% C_2H_5OH).

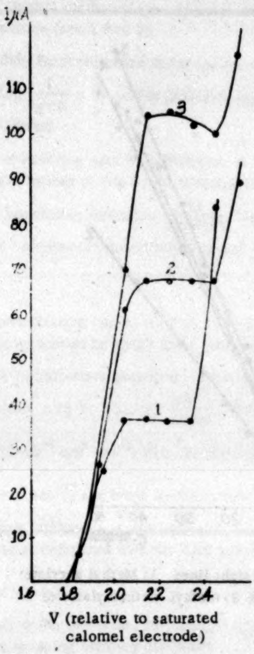


Fig. 5. Methyl methacrylate polarograms. 1) c = 15 mmol/l; 2) c = 30 mmol/l; 3) c= 45 mmol/l. Background electrolyte $(CH_3)_4NI$ (c = 0.1 m in 50% C_2H_5OH).

where D is the diffusion coefficient, $V_m = \frac{M}{d}$ is the apparent molecular volume of the substance in the solid state, M is the molecular weight, and d is the density [8].

Thus the values $D = 0.741 \cdot 10^{-5}$ cm² sec⁻¹ for methyl acrylate, $D = 0.755 \cdot 10^{-5}$ cm² sec⁻¹ for methacrylic acid, and $D = 0.69 \cdot 10^{-5}$ cm² sec⁻¹ for methyl methacrylate were found.

The n value was determined by substituting into the Ilkovic equation the values found for diffusion current at one concentration or another, the value $m^{2/3} \cdot t^{1/6}$ for the capillary constant, and the diffusion coefficient value, calculated according to the indicated method. For methyl acrylate the diffusion current value was $I_D = \frac{2.20}{0.956} = 2.26$. Hence, the value $n = \frac{I_D}{605 \cdot D^{1/2}} = 1.39$. For methacrylic acid, $I_D = \frac{1.18}{0.956} = 1.13$ and $n = \frac{1.13}{1.664} = 0.68$. For methyl methacrylate, $I_D = \frac{2.38}{1.543} = 1.54$ and $n = \frac{1.54}{1.591} = 0.96$. The fractional n values found for those ethers polarographed by the authors in the manner indicated, being different from the expected value of 2, once more indicate an irreversibility of reactions at the dropping mercury electrode.

The authors calculated diffusion coefficient values also on the basis of the experimental data obtained for diffusion current, by considering that the electron number required for reducing 1 mole of substances should be equal to 2. It follows from the Ilkovic equation that

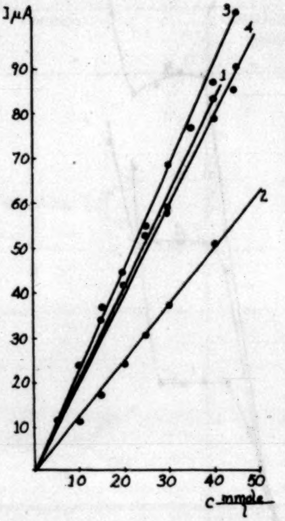


Fig. 6. Standard straight lines. 1) Methyl acrylate; 2) methacrylic acid; 3) methyl methacrylate; 4) butyl methacrylate.

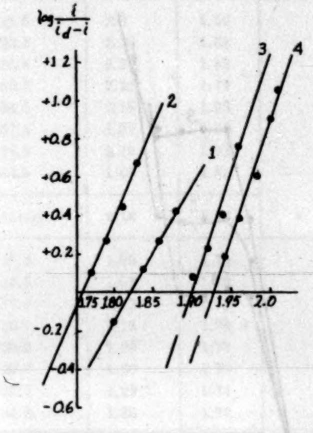


Fig. 7. Relation of $\log \frac{i}{i_d - i}$ to E. 1) Methyl acrylate; 2) methacrylic acid; 3) methyl methacrylate; 4) butyl methacrylate.

$$D = \left(\frac{I_D}{605 \cdot n}\right)^2 \text{ cm}^2\text{ sec}^{-1}.$$

Thus for methyl acrylate $D = \left(\frac{2.26}{605 \cdot 2}\right)^2 = 0.35 \cdot 10^{-5}$ cm² sec^{-1}; for methacrylic acid $D = \left(\frac{1.13}{605 \cdot 2}\right)^2 = 0.085 \cdot 10^{-5}$ cm² sec^{-1}; for methyl methacrylate $D = \left(\frac{2.38}{605 \cdot 2}\right)^2 = 0.38 \cdot 10^{-5}$ cm² sec^{-1}; and for butyl methacrylate $D = \left(\frac{2.12}{605 \cdot 2}\right)^2 = 0.31 \cdot 10^{-5}$ cm² sec^{-1}.

EVALUATION OF RESULTS

From data obtained by the authors on polarographing the esters of acrylic and of methacrylic acid, as well as the free methacrylic acid, it follows that reduction occurs at the dropping mercury electrode in the presence of a conjugated double bond for the substance in question; without this, reduction does not occur.

Laitinen and Wawzonek [7] have studied a large number of unsaturated hydrocarbons, phenyl substituted olefins and acetylenes, as well as aromatic polycyclic hydrocarbons, and have determined that isolated ethylenic and acetylenic bonds are not reduced at the dropping mercury electrode; however, double bonds conjugated with carboxyl groups, or which are present in heterocyclic compounds, analogous to pyridine or quinoline, can be reduced. Electroreduction at the dropping mercury electrode of compounds with two conjugated double bonds, in particular of esters, has been studied by Meyman and Shubenko. Korshunov and Vodzinsky [8] and a number of other authors have studied the polarographic reduction of ketones with conjugated bonds. The possibility of electroreduction at the dropping mercury electrode of unsaturated compounds with conjugated double bonds in their molecules has also been confirmed by the results of the present authors.

The resulting half-wave potentials indicate great ease in electroreduction of methacrylic acid at the dropping mercury electrode, followed next by methyl acrylate, methyl methacrylate and butyl methacrylate; reduction of these latter two esters occurs under comparable conditions (see Table 2).

Half-wave potentials obtained graphically by the authors from polarograms (at $i_d/2$) coincide well with half-wave potentials obtained from the wave equation $\left(\text{at } \log \frac{i}{i_d - i} = 0\right)$ which indicates applicability of this equation for expressing the basic electrode process as investigated.

Standard straight lines were constructed on the basis of resulting data from diffusion current values, from examination of which it follows that the increase in diffusion current of substances investigated is directly proportional to the increase in their concentration. The diffusion current constants $\frac{i_d}{cm^{2/3} t^{1/6}}$ for methacrylic acid, methyl actylate methyl and butyl methacrylates were calculated, respectively, as equal to: 1.13, 2.26, 2.38 and 2.12 $\frac{\mu A \cdot l}{mmol}$.

The function found for the diffusion current versus concentration can be used to study the polymerization kinetics of the above-named compounds, as well as for other processes in which these substances are involved.

From a comparison of data published in the literature on half-wave potentials, diffusion current constants, and diffusion coefficients values, for methyl methacrylate (2.0, 1.95 V; 1.91, 2.9 $\frac{\mu A \cdot l}{mmol}$; $0.25 \cdot 10^{-5}$, $0.573 \cdot 10^{-5}$ cm^2 sec^{-1}) and butyl methacrylate (2.0 V; 2.8 $\frac{\mu A \cdot l}{mmol}$; $0.533 \cdot 10^{-5}$ cm^2 sec^{-1}) with the data obtained by the authors for methyl methacrylate (1.90 V; 2.38 $\frac{\mu A \cdot l}{mmol}$; $0.38 \cdot 10^{-5}$ cm^2 sec^{-1}) and butyl methacrylate (1.92 V; 2.12 $\frac{\mu A \cdot l}{mmol}$; $0.38 \cdot 10^{-5}$ cm^2 sec^{-1}), it follows that the half-wave potentials, diffusion current constants and diffusion coefficient values obtained by the authors occupy an intermediate phase as compared with the data published in the literature.

SUMMARY

1. Vinyl ethers which do not possess conjugated bonds in the molecule, in $(CH_3)_4NI$ solution in 75% C_2H_5OH, or in weakly alkaline or acid medium, do not reduce at the dropping mercury electrode.

2. Methyl acrylate, methacrylic acid, methyl methacrylate and butyl methacrylate containing conjugated bonds in the molecule, in a background electrolyte of $(CH_3)_4NI$ in 50% C_2H_5OH are reduced polarographically and can be determined quantitatively.

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The resulting half-wave potentials indicate great ease in the reduction of methacrylic acid at the dropping mercury electrode, followed next by methyl acrylate, methyl methacrylate and butyl methacrylate; reduction of these latter two esters occurs under comparable conditions (see Table 5).

Half-wave potentials obtained graphically by the authors from polarograms (at $i_d/2$) coincide well with half-wave potentials obtained from the wave equation (ε, log $\frac{i}{i_d - i}$ = 0) which indicates applicability of this equation for expressing the true electrode process as irreversible.

[illegible] straight. These were constructed on the basis of resulting data from diffusion current values, the extrapolation of which, it follows that the increase in diffusion current of substances investigated is directly proportional to the increase in their concentration. The diffusion current constants $\frac{i_d}{C}$ for methacrylic acid, methyl acrylate, methyl and butyl methacrylates were calculated, respectively equal to 1.15, 2.08, 2.36 and 2.15 $\frac{\mu A \cdot l}{\text{mmol}}$.

The function found for the diffusion current versus concentration can be used to solve the polymerization kinetics of the above-named compounds, as well as the other processes in which these substances are involved.

From a comparison of data published in the literature on half-wave potentials, diffusion current constant and diffusion coefficients values for methyl methacrylate (2.8, 1.95 V; 1.95, 2.8 $\frac{\mu A \cdot l}{\text{mmol}}$; 8.23·$10^{-6}$, 8.578·$10^{-6}$ cm^2 sec^{-1}) and butyl methacrylate (2.0 V; 2.6 $\frac{\mu A \cdot l}{\text{mmol}}$; 4.632·$10^{-6}$ cm^2 sec^{-1}) with the data obtained by the authors for methyl methacrylate (1.90 V; 2.36 $\frac{\mu A \cdot l}{\text{mmol}}$; 5.08·$10^{-6}$ cm^2 sec^{-1}) and butyl methacrylate (1.93 V; 2.15 $\frac{\mu A \cdot l}{\text{mmol}}$; 4.38·$10^{-6}$ cm^2 sec^{-1}), it follows that the half-wave potentials, diffusion current constants and diffusion coefficient values obtained by the authors occupy an intermediate place as compared with the data published in the literature.

SUMMARY

1. Vinyl ethers which do not possess conjugated bonds in the molecule, in 0.1% solutions of $N(C_2H_5)_4OH$ or in weakly alkaline or acid mediums, do not reduce at the dropping mercury electrode.

2. Methyl acrylate, methacrylic acid, methyl methacrylate and butyl methacrylate containing conjugated bonds in the molecule, in a background electrolyte of $(CH_3)_4NI$ in 50% C_2H_5OH are reduced polarographically and can be determined quantitatively.

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A COMPARISON OF INVESTIGATIONAL METHODS OF COMPLEX-FORMING SYSTEMS IN ORGANIC CHEMISTRY

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In a number of investigations on the chemistry of complex organic compounds under the direction of one of the authors, various methods for detection and determination of the composition of complex compounds have been used. Results of a number of works make it possible to summarize the findings which pertain to a comparison of these methods.

I. Preparative methods, i.e., direct isolation of the complexes, and their subsequent analysis. It is possible to obtain relatively stable compounds (for example, quinhydrone, naphthalene picrate) in crystalline form by direct mixing of the component parts of the complex. At times the complex precipitates upon cooling the hot solution of one substance in the other, as for example hydroquinone and pyridine. In some cases good results are obtained by melting a mixture of the substances under investigation. Thus, the authors prepared, for example, a complex of phenol with α-aminopyridine.

To obtain unstable complexes, which at times could not be detected even by physico-chemical means, the authors successfully applied the reaction of vapors of the more volatile constituent upon crystals of the less volatile constituent. This method, popular in inorganic chemistry, as for example in the preparation of ammines, was first used by the authors during an investigation of complex-forming systems containing quinone. Thus, 16 compounds of quinone with phenols were prepared, whereas it was not possible to prepare or to identify the very unstable complexes of trichlorophenol, tribromophenol, m-cresol or 1,2,4-tribromocresol by any method.

There is described in the present work the synthesis of a series of nitrophenol complexes with amines. The method has been extended by the authors to compounds of low volatility at normal temperature. They were successfully reacted by heating. Finally, for qualitative detection of the complexes, if the latter possessed a characteristic color, grinding of the solid substances sufficed.

The method of preparing complexes based upon reaction of crystals with vapors is not suitable for substances with too low a melting point (though of course it can be extended to those substances if reaction is carried out with considerable cooling). Moreover, melting of the crystals is sometimes observed as the result of formation of a low-melting eutectic of the complex with one of the complex components [1]. In such cases, complex formation can be qualitatively determined by coloration, though the composition of the complex cannot be determined.

Finally, experiments with quinone have indicated that at times reaction between crystals and vapors does not occur in those compounds which form a definite complex in solution. This phenomenon was observed with anthracene, phenanthrene, acenaphthene and dibenzylsulfide. For the compounds enumerated, complex formation with quinone was proved colorimetrically, and others by thermal analysis. Apparently the quinone molecules cannot penetrate into the crystalline lattices of other substances.

II. Methods of Physico-Chemical Analysis, of which the Following were used by the Authors

1) The classical method of thermal analysis. Complex formation of phenols, carboxylic acids, organic sulfides, nitro compounds, amines, and amides was studied in various combinations. New complexes were found, but on the whole the method was not very sensitive. Instability of many compounds to heat was evident.

2) Colorimetric analysis. This was introduced for the first time into the chemistry of organic complexes by Ostromyslensky [2]. The method was applied by the authors in a rough form, using a Dubosq colorimeter. As indicated by complex formation of nitro compounds with amines, which was studied in particular, colorimetric measurement led to positive results for many systems where the melting diagrams did not exhibit chemical interaction. In experiments with nitro compounds and amines, this phenomenon occurred in 6 cases, but in only three systems (α-nitronaphthalene—aniline, m-dinitrobenzene—aniline, m-dinitrobenzene—benzidine) did both methods give positive results, as well as indicate identical compositions for the complexes [1].

3) The electrochemical method. This method was developed at the Tomsk Polytechnic Institute organic chemistry laboratory, based upon a determination of current density in a closed circuit, where the source of energy was the reaction of the compound under investigation, or of the mixture, with metal [3]. Measurement was carried out by means of a sensitive galvanometer with high resistance. The current density values read on the galvanometer depend upon the EMF appearing during reaction, and upon electroconductivity of the system under study. Polarization also exerts an influence. Experiments have indicated, however, that during investigation of organic compounds the method in question can give a good characterization of reactivity with respect to metals. In studying complex formation, the method was found to be very sensitive, if, of course, reaction occurs with metals [4].

More than 200 systems were investigated, and more than 100 complexes determined, many of which failed to be detected by the melting diagrams. Some complexes were then isolated, and their compositions determined entirely, or almost so, for those compositions corresponding to maximum deviation of the galvanometer needle. It also became apparent that the value shown by the millivoltmeter characterized the molecular compound better than did the electroconductivity of the mixture.

In the experimental part of the authors' work, complex formation between phenols and the aromatic and heterocyclic amines is described. Investigation was carried out by the preparative procedure in various modifications, and by two physico-chemical methods of analysis: fusion diagrams, and electrochemically, according to Tronov and Kulev. The authors attempted to apply both methods to the same systems.

Eight complexes were isolated by the preparative method in various modifications. The principal complex formers were benzidine (3 complexes), α-aminopyridine (3 complexes), and β-naphthylamine (2 complexes). Composition of one benzidine and of both naphthylamine complexes corresponded to a ratio of 1 : 1 for phenolic hydroxyl : amino group, i.e., complex formation in this case should proceed according to the standard acid-amine manner. In one complex a polyhydroxy phenol reacted with benzidine, but not with all of the hydroxyls. Trichlorophenol possessed an unusual composition with benzidine, in which two hydroxyls were assigned to one amino group. Composition of the phenols with aminopyridine compounds was variable. Aminopyridine possesses two nitrogens, and either one or both can enter into reaction. Complexes are possible between aminopyridine and nitrophenols, and bonds of amino nitrogen with hydroxyl or with nitro groups, as indicated by retention of a light-yellow color in the former and deepening of the color in the latter.

TABLE

No.	System	By the Tronov-Kulev electrochemical method	Complexes, found			
			by thermal method of analysis	by viscosity	by electroconductivity	by preparatory method
1	Phenol—aniline	1:1 2:1	1:1 [8]	2:1 [8]	1:1 [11], 1:2 [10]	1:1 [12], 2:1 [13]
2	Phenol—dimethylaniline	—	— [9]	s-shaped curve		
3	Phenol—α-naphthylamine	1:1 4:1	1:1 [16]			1:1 [18]
4	Phenol—pyridine	1:1	1:1, 2:1 [8]			1:1, 2:1 [17]
5	Phenol—α-aminopyridine	2:1	1:1			1:1
6	o-Chlorophenol—aniline	1:1	1:1 [14]			
7	o-Chlorophenol—dimethylaniline	—	1:1 [14]			
8	o-Chlorophenol—pyridine	2:3, 1:1	1:1 [14]	4:1		
9	o-Chlorophenol—α-aminopyridine	1:1, 2:1				2:1
10	o-Chlorophenol—quinoline	1:1, 3:2	1:1 [14]			
11	o-Nitrophenol—α-aminopyridine	1:1	—			
12	α-Naphthol—pyridine	1:1	Does not crystallize, vitreous mass.	2:1 [19]	2:1 [19]	
13	α-Naphthol—quinoline	1:1	1:1, 1:2 [15]	1:1 [15]	1:1 [15]	
14	β-Naphthol—pyridine	2:3, 2:1		2:1 [19]	2:1 [19]	
15	β-Naphthol—quinoline	1:1, 2:1	1:1, 2:1 [15]	2:1 [15]	2:1 [15]	

Note: First number = number of phenol molecules; second number = number of amine molecules; dash = no interaction.

It is to be regretted that results obtained by the preparative investigation method could not always be compared with the physico-chemical method of analysis, and especially with the electrochemical analysis according to Tronov and Kulev, since the last method was of particular interest to the authors. Electrochemical analysis required the use of solvents in which some of the phenols are poorly soluble; in the table, therefore, in which a comparison of methods is made, only a few investigational results are given. For the phenols and amines enumerated in the table, complete data on the investigation of these compounds by the method of Tronov and Kulev, and a considerable amount of data by the thermal method of analysis are available. Data found in the literature for the electroconductivity and viscosity of these same systems are also included.

The table indicates a somewhat higher sensitivity for the Tronov-Kulev method. If 12 systems be taken, in which this last method and thermal analysis are applied, there then will be found electrochemically 15 complexes, and by thermal analysis, 13 complexes. From their compositions, 9 coinciding complexes were found, 6 were found by electrochemical analysis only, and 4 thermally; in one case (phenol–dimethylaniline) both methods led to negative results. Measurements of viscosity and of electroconductivity frequently yielded the same results as with the preceding two methods, but at times indicated a fewer number of complexes, and at times also made possible the detection of new complexes. On the whole, however, comparison here remains quite fragmentary.

In general, none of the methods for investigating complex formation can be considered to be favored over all the others. Each method has its area of application, which is defined by the properties of all of the compounds studied. The colorimetric method is very sensitive, but applicable only in those cases where upon formation of a complex there is an appearance of, or a change in, coloration. In the electroconductivity determination there is the requirement that the system not possess a very low electroconductivity. The electrochemical method, as developed in the Soviet Union, is based upon reaction with metals, but not all organic substances are capable of reaction with metals; furthermore, the likelihood of obtaining good results is related to the solubilities of the compounds used in the solvents required for the work.

Finally, there should be taken into account the fact that the formation of any complex may have differing influences upon indices determined by physico-chemical analysis; so, at times in the same system, one method indicates a complex of a given composition, the formation of which has a more pronounced effect on that specific property of the substances, while the characterizing curve obtained by use of another physical index shows particular points at other places. So, for a complete study of any one system with respect to formation of complexes, several methods should be used.

EXPERIMENTAL

I. Isolation of Complexes from Solutions and from Melts

1. Phenol–α-aminopyridine. The complex crystallized slowly from the melt of equimolecular amounts of the starting substances. Large elongated platelets, white in color, washed with benzene, melted at 21-22°.

0.2265 g sub.: 23.60 ml 0.1 N H_2SO_4. 0.2520 g sub.: 25.59 ml 0.1 N H_2SO_4. Found %: N 14.64, 14.28 (according to the Kjeldahl modified method [5]). $C_6H_5OH \cdot C_5H_4N(NH_2)$. Calculated %: N 14.85.

2. o-Chlorophenol–α-aminopyridine. The compound was obtained in an identical fashion. The white precipitate which formed, possessed a m.p. of 42-43.5° after 2 washings with small amounts of benzene. Complex volatile in air.

0.1902 g sub.: 0.1640 g AgCl. 0.1932 g sub.: 0.1632 g AgCl. 0.2454 g sub.: 12.10 ml 0.1 N H_2SO_4. 0.2600 g sub.: 13.34 ml 0.1 N H_2SO_4. Found %: Cl 21.60, 20.94; N 6.90, 7.18. $2C_6H_4ClOH \cdot C_5H_4N(NH_2)$. Calculated %: Cl 20.23; N 7.97.

3. p-Nitrophenol–α-aminopyridine. Upon mixing the benzene solution, fine yellow crystals precipitated, which, after washing with benzene and drying, had a m.p. of 89-90°. The complex was stable in air.

0.1366 g sub.: 14.70 ml 0.1 N H_2SO_4. 0.1336 g sub.: 14.80 ml 0.1 N H_2SO_4. Found %: N 15.06, 15.50. $[C_6H_4NO_2OH]_2 \cdot C_5H_4N(NH_2)$. Calculated %: N 15.04.

4. Pyrogallol–benzidine. Formed during mixing of benzene solutions at a ratio of 1:1 for pyrogallol to benzidine. White, elongated, hexagonal platelets, with m.p. 143-144.5°.

0.4110 g sub.: 26.83 ml 0.1 N H_2SO_4. 0.4106 g sub.: 27.20 ml 0.1 N H_2SO_4. Found %: N 9.11, 9.29. $C_6H_3(OH)_3 \cdot (C_6H_4NH_2)_2$. Calculated %: N 9.00.

The molecular ratio of initial substance at 2:1 led to formation of the same compound, and some crystals of different form, composition not characterized. The melting diagram for the system had 3 maxima, corresponding to the compositions 1:1, 2:1 and 3:2 (the first number indicating number of pyrogallol molecules).

5. Phloroglucinol—benzidine. The complex precipitated from aqueous solution. White, rhomboidal platelets with m.p. 164-167°. Readily soluble in alcohol and acetone, less so in ether and poorly so in cold water.

0.4096 g sub.: 30.55 ml 0.1 N H_2SO_4. 0.4130 g sub.: 31.53 ml 0.1 N H_2SO_4. Found %: N 10.45, 10.68. $2C_6H_3(OH)_3 \cdot 3(C_6H_4NH_2)_2$. Calculated %: N 10.44.

6. 2,4,6-Trichlorophenol—benzidine. The purest complex resulted from a benzene solution at a molecular ratio of 6:1 for trichlorophenol to benzidine. Needle crystals, with m.p. 99-100°. Readily soluble in chloroform, alcohol, ether. It lost trichlorophenol to the air slowly.

0.1678 g sub.: 3.68 ml 0.1 N H_2SO_4. 0.1430 g sub.: 3.00 ml 0.1 N H_2SO_4. 0.1026 g sub.: 0.1793 g AgCl. 0.0794 g sub.: 0.1378 g AgCl. Found %: N 3.07, 2.93; Cl 43.30, 43.54. $4C_6H_2(OH)Cl_3 \cdot (C_6H_4NH_2)_2$. Calculated %: N 2.87; Cl 43.75.

7. 2,4-Dichlorophenol—α-naphthylamine. The complex resulted upon mixing saturated benzene solutions together in equimolecular amounts. Needle crystals, m.p. 72-73°. Soluble in benzene, ether and chloroform. Decomposed by hot water. Gradually lost dichlorophenol to the air.

0.1868 g sub.: 6.60 ml 0.1 N H_2SO_4. 0.2144 g sub.: 7.60 ml 0.1 N H_2SO_4. 0.1618 g sub.: 0.1500 g AgCl. 0.1914 g sub: 0.1777 g AgCl. Found %: N 4.94, 4.96; Cl 22.92, 23.01. $C_6H_3(OH)Cl_2 \cdot C_{10}H_7NH_2$. Calculated %: N 4.57; Cl 23.20.

8. 2,4,6-Trichlorophenol—β-naphthylamine. 0.02 mole of trichlorophenol was added, with stirring, to 0.02 mole of β-naphthylamine in 40 ml of benzene; complete dissolution of components was effected. After a half-hour, a flaky precipitate began to form. It was washed with benzene and dried at 50°; m.p. 94-96°. The complex was soluble in benzene, alcohol and chloroform. It lost trichlorophenol in the air.

0.4024 g sub.: 12.58 ml 0.1 N H_2SO_4. 0.4012 g sub.: 12.12 ml 0.1 N H_2SO_4. 0.1532 g sub.: 0.1922 g AgCl. 0.1486 g sub.: 0.1858 g AgCl. Found %: N 4.39, 4.22; Cl 31.03, 31.90. $C_6H_2(OH)Cl_3 \cdot C_{10}H_7NH_2$. Calculated %: N 4.11; Cl 31.25.

II. Preparation of Complexes by Heterogeneous Reactions

The systems studied were those in which nitrophenol on the one hand, and amines of low volatility on the other, were used. Nitrophenols were particularly suited to the method in question since they produced bright-colored compounds, whose presence was easy to detect. For a majority of the systems first taken, the authors carried out the qualitative test by grinding the crystals. For the quantitative investigation, beakers containing the reacting components were placed in an apparatus consisting of small desiccator, placed in a thermostatic box, equipped with contact thermometer. After a specified interval, the beaker, with non-volatile substance, was weighed. Thus the reaction rate was determined, and in those cases where a crystalline product resulted, the weight gain could be determined as well as the composition of the complex. Complex formation was accelerated upon continuous stirring of the crystals.

1. 2,4-Dinitrophenol + α-aminopyridine. Reaction temperature was 50°. The resulting bright-red crystals melted at 154-155°, and after crystallization from chloroform, had a m.p. of 156-157°. Stable in air. Decomposed by acid and alkalies.

0.1530 g sub.: 22.15 ml 0.1 N H_2SO_4. 0.1454 g sub.: 21.20 ml 0.1 N H_2SO_4 (according to the modified Kjeldahl method). Found %: N 20.26, 20.34. $C_6H_3(NO_2)_2OH \cdot C_5H_4N(NH_2)$. Calculated %: N 20.14.

The same data were obtained by the quantity of aminopyridine added (experiment continued until beaker with dinitrophenol reached constant weight), i.e., by the gain in weight: 0.5000 g of dinitrophenol gave 0.7567 g of complex; for a complex of the indicated composition, 0.7556 g is required, i.e., 100.14% of theory was obtained.

2. 2,5-Dinitrophenol + α-aminopyridine. Temperature 50°. The complex was in the form of carmine-red needles with m.p. 150°. After recrystallization from benzene, it melted at 151-152°. Stable in air. Decomposed by water and acids. Soluble in hot benzene or chloroform, with disappearance of the red color, but upon cooling, precipitated in the previous form.

0.1222 g sub.: 17.78 ml 0.1 N H_2SO_4. 0.0840 g sub.: 15.94 ml 0.1 N H_2SO_4. Found %: N 20.38, 19.90 (according to Kjeldahl). $C_6H_3(NO_2)_2OH \cdot C_5H_4N(NH_2)$. Calculated %: N 20.14.

0.500 g of dinitrophenol: weight of complex 0.7556 g. Calculated: 0.7556 g. Found: 99.86% of theory.

Upon stirring the complex with 2,4,6-trinitrophenol crystals, the color gradually changed to yellow as a result of aminopyridine picrate formation.

3. 2,6-Dinitrophenol + α-aminopyridine. Conditions the same. Orange needle crystals resulted with m.p. 198-198.5°. Recrystallized from benzene and chloroform. Decolorized by ethyl alcohol and sulfuric acid. Stable in air. As with preceding, slowly sublimed above 50°.

0.1100 g sub.: 16.00 ml 0.1 N H_2SO_4. 0.1216 g sub.: 17.68 ml 0.1 N H_2SO_4. Found %: N 20.36, 20.05 (according to Kjeldahl). $C_6H_4(NO_2)_2OH \cdot C_5H_4N(NH_2)$. Calculated %: N 20.14.

0.5000 g of dinitrophenol: 0.7532 g is the weight of complex. Calculated: 0.7558 g. Found: 99.68% of theory.

Color of the complex with trinitrophenol changed to yellow.

4. p-Nitrophenol + α-aminopyridine. Temperature was 50°. The substance melted during the reaction.

5. p-Nitrophenol + pyridine. The experimental temperature was 15-17°. Lemon-yellow crystals with m.p. 63-64° resulted, which is in accordance with the literature data [6].

0.5000 g of nitrophenol: 0.7929 g is the weight of the complex. $C_6H_4(NO_2)OH \cdot C_5H_5N$. Calculated: 0.7842 g. Found: 101.1% of theory.

6. 2,4-Dinitrophenol + pyridine. Temperature 15-17°. Light-orange crystals with m.p. 79-80° resulted. The complex, as with the preceding one, slowly lost pyridine.

0.5000 g of dinitrophenol: 0.7208 g is the weight of the complex. $C_6H_3(NO_2)_2OH \cdot C_5H_5N$. Calculated: 0.7158 g. Found: 100.69% of theory.

Upon mixing with aminopyridine, there gradually formed the complex already described of the latter with dinitrophenol.

7. 2,4-Dinitrophenol + α-aminopyridine. The experiment was carried out with continuous stirring of the crystals of reacting substances. Temperature was 50°. The mixture was analyzed from time to time by washing away the aminopyridine with carbon tetrachloride and drying the residue at 45° to constant weight. The complex, m.p. 153-155°, described earlier, resulted, but the reaction was 98% complete after 2.5 hours, while with the previous synthetic method it was continued for 28 days.

By the same method, 2,4-dinitrophenol was reacted with non-volatile amines: α-naphthylamine, β-naphthylamine, benzidine. The properties of the complexes coincided with the properties as described in the literature [7].

III. A Study of Complex Formation by the Thermal Analysis Method

The apparatus used for thermal analysis consisted of a test tube equipped with stirrer and calibrated thermometer, glass sleeve for uniform heating and cooling of the substance in the tube, and a glycerine bath. Calculations for the components was carried out in mol. %. Experiments were usually set up with ratios differing by 10% from each other. For some parts of the diagram, points were plotted more frequently.

The batches of substances taken were placed in the tube and melted. Then, with cooling and constant stirring of the melt, the temperature of the liquid mixture was determined every minute and especially the temperature for first appearance of crystals, and for eutectic crystallization. In the systems with α-aminopyridine, cooling was carried out with snow and cooling mixture. Supercooling was avoided by vigorous stirring and the use of seeders. Results obtained are given in Figs. 1, 2 and 3.

IV. A Study of Complex Formation by the Tronov-Kulev Electrochemical Method

The experiments were carried out in an apparatus as described by the authors of the method [3]. Its construction is given in Fig. 4, where (1) is a metallic cylinder with hard rubber sleeve; (2) is a platinum crucible; (3) is a hard rubber cover, tightly sealing the cylinder; (4) is a metal plug; (5) is a contact plate; (6) and (7) are the brass rod with pointed tip for sodium electrode; (8) is a glass socket; (9) is the mobile contact; (10) the

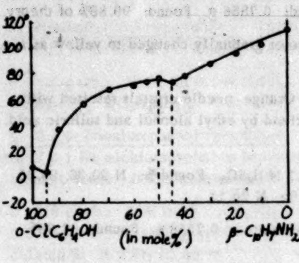

Fig. 1. o-Chlorophenol—β-naphthalene system.

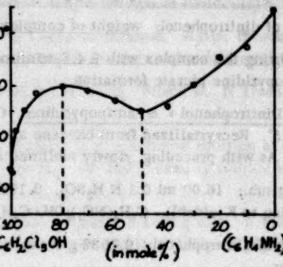

Fig. 2. Trichlorophenol—benzidine system.

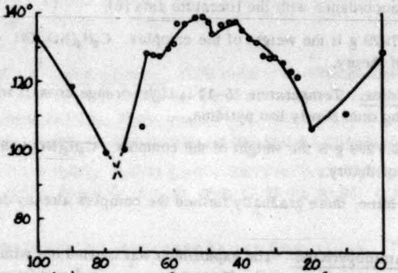

Fig. 3. Pyrogallol—benzidine system.

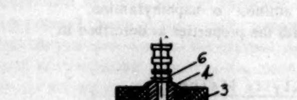

Fig. 4. Exaplanation in text.

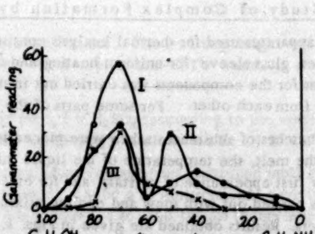

Fig. 5. Phenol—aniline system. I) Concentration 1:40 M; II) concentration 1:40 M, temperature 43°; III) concentration 1:80 M.

outlet plates for connection with galvanometer. The length of the glass sleeve was such that the pressed sodium electrode protruded only about $^3/_4$ of the way out of the socket, and the remaining portion was tightly sealed from access of liquid inside the socket.

The substances investigated, taken in specific molar ratios, were placed in the platinum crucible, and benzene added to total volume of 6 ml. The crucible, which also served as one electrode, was lowered into the hard rubber socket of the metallic cylinder, from the bottom of which through an outlet (10) was attached the galvanometer. Then, by means of the ground end of the glass socket, fastened into the hard rubber cover, there served as the second electrode a small cylinder cut from sodium, 6 mm in diameter and 9 mm long, the cover being placed into cylinder (1). The sodium was pressed out into the liquid by a brass rod connected, through the plate (5), with the other galvanometer contact. At the same time, galvanometer readings were taken at specific time intervals: 30 sec, 1 min, 2 min, and so forth.

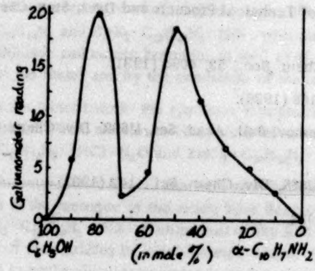

Fig. 6. Phenol–α-naphthylamine system.

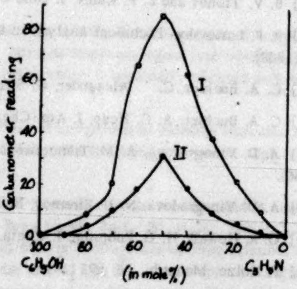

Fig. 7. Phenol–pyridine system. I) Concentration of 1:60 M; II) concentration of 1:80 M.

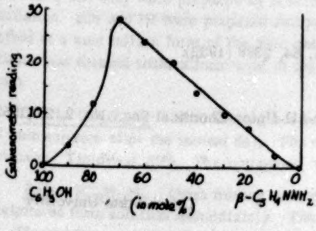

Fig. 8. Phenol–α-aminopyridine system.

A galvanometer of the S-IV type from the Physics Institute of the Leningrad University was used, with a resistance of 2800 ohms, and a scale of 45 mV. For each ratio maximum, readings were taken on the galvanometer and curves plotted according to the data. From the character of the curves, conclusion could be drawn as to the composition of the complexes being formed. As a rule, experiments were carried out at 15-17°, some other systems being studied at higher temperature and different concentrations.

The experimental results are presented in the table and in Figs. 5, 6, 7 and 8.

SUMMARY

1. A comparison of several methods of studying complex forming systems has been carried out. Systems composed of phenols and amines have been studied experimentally. Methods of investigation have been: direct isolation of the complexes, with chemical analysis of the latter and physico-chemical analysis.

2. Eight new complexes have been isolated and analyzed. During the preparation of the complexes, good results have been obtained by the method of heterogenic reactions. Crystals of non-volatile components of the system have reacted with vapors of the volatile component.

3. Of the various available physico-chemical methods, the methods of thermal analysis and of Tronov and Kulev's electrochemical procedure based upon determination of current density, in a closed circuit where the energy source is the reaction of the substance studied with metal, have been utilized. This latter method has been found to be somewhat more sensitive.

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COMPOUNDS OF ZINC HALIDE WITH NICOTINE*

S. F. Babak and I. A. Kondrashov

In the preceding works [1, 2] the authors have demonstrated that nicotine forms two types of compounds: $HgX_2 \cdot C_{10}H_{14}N_2$ and $HgX_2 \cdot C_{10}H_{14}N_2 \cdot 2HX$, with mercury halides. Nictone forms analogous type compounds with cupric chloride and cupric bromide, as well as of another composition which is apparently affected both by the nature of the metal and by the conditions of the reaction course.

In the present work the synthesis, composition, and properties, of compounds of nicotine with zinc halides are described. With respect to compounds of nicotine with zinc halides, the following are known: $ZnI_2 \cdot C_{10}H_{14}N_2$, $ZnCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl \cdot H_2O$ and $ZnCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl \cdot 4H_2O$ [3].

The interaction of nicotine with zinc halides has been studied in acetone by the authors, and in aqueous solutions in the presence of the acids; here three compound have been found: $ZnX_2 \cdot 2C_{10}H_{14}N_2$, $ZnX_2 \cdot C_{10}H_{14}N_2 \cdot HX$ and $ZnX_2 \cdot C_{10}H_{14}N_2 \cdot 2HX$. Compounds of the first type result from mixing of anhydrous acetone solutions of nicotine and of zinc halides in stoichiometric ratios. Compounds of the second type are formed upon mixing aqueous solutions in equimolecular quantities, as they enter into the composition of the components. The third type of compound results upon mixing zinc halides and nicotine in a 1:1 ratio and in a highly acid aqueous medium of the corresponding hydrogen halides. Compounds of the first and third types result with a small excess of nicotine.

The nicotine boiled at 111-112° (6 mm), d_{25} 1.0068, η_{25} 3.8942. Dry acetone was used, $ZnCl_2$ – chemically pure, $ZnBr_2$ and ZnI_2 were prepared by reacting ZnO with hydrobromic and hydriodic acids. HCl was purified by distillation. HBr and HI were prepared and purified by standard methods. Zinc was determined by the weight method as a zinc sulfate form of the zinc oxide; halides were determined according to Volhard as silver halides, nicotine was titrated with sulfuric acid in the presence of methyl red, after distilling from alkaline solution with steam.

$ZnCl_2 \cdot 2C_{10}H_{14}N_2$. After mixing acetone solutions of zinc chloride and nicotine, white crystals precipitated from solution after the second day. The crystals were filtered off, washed with acetone and dried in a vacuum desiccator. Yield was 85%. The compound melted with decomposition at 138-140°.

$ZnBr_2 \cdot 2C_{10}H_{14}N_2$. Upon mixing acetone solutions of zinc bromide and of nicotine, white fine, crystals precipitated from solution immediately. The crystals were filtered off, washed with ether and dried in a desiccator. The resulting compound melted at 148-150° with decomposition. Yield was 87%.

$ZnI_2 \cdot 2C_{10}H_{14}N_2$. The preparational method for this compound was similar to the preceding. The white, crystalline substance melted with decomposition at 125-126°. Yield was 91%.

$ZnCl_2 \cdot C_{10}H_{14}N_2 \cdot HCl$. The compound resulted from mixing aqueous solutions consisting of equimolecular amounts of zinc chloride, hydrochloric acid and nicotine. Fine, white crystals immediately formed in solution. The crystals were filtered off by suction, washed with water, and dried. Melted with decomposition at 241-246°. Yield was 89%.

$ZnBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$. Prepared in the same manner as preceding. The white crystals melted with decomposition at 257-260°. Yield was 90%.

$ZnBr_2 \cdot C_{10}H_{14}N_2 \cdot 2HBr$. The compound resulted on mixing equimolecular amounts of aqueous solutions of zinc bromide and nicotine in the presence of a large amount of hydrobromic acid. The solution was concentrated with charcoal and filteredd while hot. Upon cooling, white crystals precipitated from the filtrate, which were separated on a Schott filter, washed with cold water and dried in a desiccator. The compound melted with decomposition at 214-216°, Yield was about 77%.

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* N. Kalustova participated in the experimental part.

$\underline{ZnI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI}$. The compound was formed by mixing aqueous solutions of zinc iodide and nicotine in 1:1 ratio in the presence of a large amount of hydriodic acid. There precipitated immediately from solution slightly-yellow crystals, which were separated and washed with a small amount of cold water; with such procedure they became white, and again yellow when stored in a desiccator due to their partial decomposition by separation of iodine. Melting with decomposition at 237-238°. Yield about 30%.

TABLE

Analytical Results for Compounds Obtained

No.	Compound	Melting point	Nicotine (%)		Zinc (%)		Halide (%)	
			found (average)	calculated	found (average)	calculated	found (average)	calculated
1	$ZnCl_2 \cdot 2C_{10}H_{14}N_2$.	138-140°	70.08	70.41	13.64	13.38	15.66	15.39
2	$ZnBr_2 \cdot 2C_{10}H_{14}N_2$.	148-150	59.10	59.01	11.61	11.89	29.13	29.09
3	$ZnI_2 \cdot 2C_{10}H_{14}N_2$.	125-126	50.42	50.38	10.11	10.16	40.08	39.44
4	$ZnCl_2 \cdot C_{10}H_{14}N_2 \cdot HCl$	241-246	48.48	48.55	19.46	19.52	31.14	31.76
5	$ZnBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$	257-260	34.53	34.62	13.82	13.96	51.22	51.19
6	$ZnBr_2 \cdot C_{10}H_{14}N_2 \cdot 2HBr$.	214-216	29.54	29.52	11.82	11.89	57.94	58.17
7	$ZnI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI$	237-238	21.41	21.72	8.68	8.86	69.01	68.86

Compounds of zinc halide with nicotine containing no acid in their composition are poorly soluble in water. $ZnCl_2 \cdot 2C_{10}H_{14}N_2$ dissolves in methyl and ethyl alcbhols; $ZnBr_2 \cdot 2C_{10}H_{14}N_2$ dissolves in methyl but does not dissolve in ethyl alcohol. Both are poorly soluble in ether and acetone. $ZnI_2 \cdot 2C_{10}H_{14}N_2$ does not dissolve in the indicated solvents. Acid-containing compounds of zinc halide with nicotine are soluble in water and insoluble in ether, acetone, methyl and ethyl alcohols. All compounds described dissolve readily in hydrobromic, hydrochloric and hydriodic acids; as well as in nitric acid.

SUMMARY

Crystalline compounds of nicotine with zinc halides have been prepared as follows: $ZnCl_2 : 2C_{10}H_{14}N_2$, $ZnBr_2 \cdot 2C_{10}H_{14}N_2$, $ZnI_2 \cdot 2C_{10}H_{14}N_2$, $ZnCl_2 \cdot C_{10}H_{14}N_2 \cdot HCl$, $ZnBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$, $ZnBr_2 \cdot C_{10}H_{14}N_2 \cdot 2HBr$ and $ZnI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI$.

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A STUDY OF CHITIN

I. ACTION OF ACIDS AND OF ALKALIES UPON CHITIN

S. N. Danilov and E. A. Plisko

It has been determined by chemical [1-4] and by physical [5, 6] investigations that chitin consists of monoacetylglucosamine residues joined by 1,4-β-glucosidyl bonds, with 180° rotation. Thus the chitin macromolecule is constructed analogously to that of cellulose, but differs from the latter in that hydroxyl groups at the C_2 atoms are substituted by aminoacetyl groups, which apparently accounts for the differing properties of cellulose and chitin. As with cellulose, chitin is insoluble in water and organic solvent; in contrast to cellulose, it does not dissolve in ammoniacal copper solution, and swells but very little with rise in temperature.

Treatment of chitin with sodium hydroxide or potassium hydroxide at high temperature (up to 180°) leads to deacetylation and destruction of chitin, the so-called chitosan which results possessing different properties from that of chitin (Gilson [7], Hoppe-Seyler [8]).

Chitosan prepared in such a manner [9] is obtained as a yellow, amorphous mass, insoluble in water and alkalies; readily soluble in dilute hydrochloric acid and acetic acid, and precipitated from these solutions by alkalies. Chitosan is found to be one of the products of extensive disintegration, and possibly oxidation, of chitin, data for which have been obtained by various authors [10, 11].

The present authors have used low temperature in order to avoid possible oxidation in the splitting of chitin in experiments concerning the relationship of chitin to alkalies.

It is known that the swelling of polysaccharides is an exothermic process; according to LeChatelier's principle, lowering of the temperature should favor an increase in swelling, which is confirmed by experiments (negative temperature coefficient of swelling).

Nikitin and coworkers have developed a method for freezing cellulose in alkalies and low molecular weight xanthogenates in 8% sodium hydroxide [12]. Taking into account the analogy in structure for chitin and cellulose, it can be postulated that decrease of temperature will result in an increased swelling in alkaline solutions, which has also been indicated by preliminary experiments described in the literature [13].

The authors have established that on cooling of alkaline solution down to freezing, with subsequent thawing, there is observed not just swelling of chitin upon its dissolution. Chitin samples separated after treatment of alkalies of various concentration, and at lowered temperature, have even swelled without limit (dissolved) in dilute organic and mineral acids. Analysis of the isolated samples for acetyl content has indicated that their content is considerably decreased because of hydrolysis under the conditions of alkali treatment. Preparations obtained by the authors, however, are still closely related to chitin and differ from chitosan described in the literature. More complete swelling of chitin in alkalies might be attributed to removal of acetyl groups, but chitin samples separated after treatment with alkalies did not swell at room temperature. Swelling at low temperature is apparently conditioned not by splitting off of acetyl groups, but by loosening the chitin strand structure.

Because of the fact that in treatment of chitin by alkali at low temperature there occurs considerable hydrolysis of acetyl groups, there then appear primary amino groups whose percentage content has been determined by the Van Slyke method [14]. The authors, however, did not succeed in completely removing acetyl groups to obtain the corresponding aminopolysaccharide.

The relationship of chitin to acids has received but little illumination in the literature.

Sulfuric (70-79%) [2] and hydrochloric [1, 3] acids have been used primarily for elucidation of the chitin structure.

It is known from the works of Eckenstamm [15] that the rate constant for cellulose hydrolysis in strong phosphoric acid is 200-fold less than in strong sulfuric acid; the authors therefore proposed to use phosphoric acid as the solvent in molecular weight determination by the viscometric method, and for fractionating cellulose. The authors have carried out experiments on dissolution of chitin in phosphoric acid, and the properties of the solutions and of chitin regenerated from solution have been studied.

Meyer and Wehrli have indicated [11] that phosphoric acid dissolves chitin at concentrations from 45 to 85% within an hour.

A thorough study of the authors' chitin samples with respect to solubility in phosphoric acid established that 40, 50 and 60% phosphoric acid does not dissolve chitin, even upon prolonged reaction time (up to 6 days). Partial dissolution was observed at concentrations from 70.10 to 76.73%, and complete dissolution took place at acid concentrations from 78.4 to 97.2% (Fig. 1). The authors have determined characteristic viscosities of chitin in phosphoric acid.

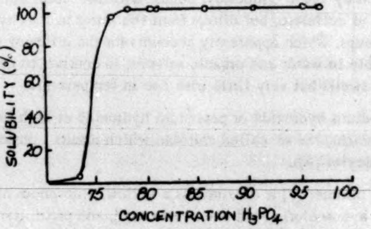

Fig. 1. Solubility of chitin in phosphoric acid

TABLE 1

Chemical composition of crab and crayfish chitin

Crude material	Sample number	Content found minus ash (in %)				Ash (in %)	Crude material	Sample number	Content found minus ash (in %)				Ash (in %)
		C	H	N	CH_2CO								
Crab chitin	1	46.96	6.65	6.68	20.02	0.23	Crayfish chitin	1	46.91	6.65	6.58	20.05	0.23
	2	46.72	6.67	6.70	20.30	0.14		3	46.76	6.82	6.24	19.94	0.33
	3	46.66	6.75	6.52	20.06	0.32		5	46.83	6.37	–	20.28	0.24
	4	46.95	6.77	6.48	19.80	0.14		6	46.92	6.70	6.65	20.28	0.22
	5	46.55	6.75	6.73	19.85	0.66							
	6	46.72	6.69	6.51	19.85	0.09							

Note: Theoretical content for $(C_8H_{13}O_5N)_n$ in %: C 47.27; H 6.40; N 6.89; CH_3CO 21.13.

EXPERIMENTAL

Chitin for the experiments was obtained by the authors from crab shells (Far East) and from local crayfish [16-19]. The shells were cleaned of muscle remains and then ground in a rotary mill. The ground shell was then sifted through a set of sieves; shell of varying degrees of pulverization were thus obtained. The resulting shell was treated first with water and then with 5% hydrochloric acid. Following this, disintegration of protein and pigment substances was carried out by boiling the shell in a 5% solution of sodium hydroxide for 4 hours. The isolated chitin was washed repeatedly with water and dried at 105°. The pigment residue was removed by extracting with alcohol and benzene (1 : 1) mixture in a Soxhlet apparatus. The isolated chitin samples were of the chemical compositions given in Table 1.

Action of Alkalies upon Chitin

Chitin samples, obtained according to the above described procedure, were treated with alkali solutions of various concentrations at various temperatures. Experiments at −10, −20, −30 and −40° were carried out in a freezer with automatic temperature regulator and at −70° in a Dewar flask with solid carbon dioxide. It can be seen from

TABLE 2

Experiments on Treatment of Chitin at Various Alkali Concentrations at Low Temperatures

Sample No.	Experimental conditions	Properties of Chitin Samples after treatment with alkali
	Chitin treated with 4% NaOH	
1	At −10°; 8 hours, ratio 1 : 10	Samples 1-3 did not swell in concentrated or dilute organic acids. They dissolved in 60% H_2SO_4, 50.70% HNO_3, 37% HCl, 78.4 and 97% H_3PO_4. Sample 4 swelled a little in dilute acetic and formic acids. Soluble in concentrated mineral acids.
2	At −20°; 10 freezings, ratio 1 : 15	
3	At −30°; 14 freezings, ratio 1 : 15	
4	At −40°; 14 freezings, ratio 1 : 15	
	Chitin treated with 8% NaOH	
5	At −10°; 8 hours, ratio 1 : 10	Samples 5-7 had the same properties as samples 1-3. Samples 8, 9 and 13 swelled a great deal in dilute organic and mineral acids. Samples 10-12 dissolved in dilute 2-10% organic and mineral acids.
6	At −10°; 8 hours, ratio 1 : 10	
7	At −20°; 10 freezings, ratio 1 : 15	
8-9	At −30°; 14 freezings, ratio 1 : 15	
10-12	At −40°; 14 freezings, ratio 1 : 25	
	Chitin treated with 10% NaOH	
13	At −30°; 14 freezings, ratio 1 : 15	Samples 14 and 15 dissolved in dilute organic acids.
14-15	At −40°; 14 freezings, ratio 1 : 15	
	Chitin treated with 19.5% NaOH	
16	At −40°; 14 freezings, ratio 1 : 15	Samples 16, 17 swelled greatly and dissolved partially in dilute organic and mineral acids. Soluble in concentrated mineral acids.
17	At −70°; 14 freezings, ratio 1 : 15	
	Chitin treated with 30% NaOH	
18	At −30°; 14 freezings, ratio 1 : 15	Samples 18-20 swelled greatly in dilute organic acids; soluble in concentrated mineral acids.
19	At −40°; 14 freezings, ratio 1 : 15	
20	At −70°; 14 freezings, ratio 1 : 15	

TABLE 3

Amino Nitrogen in Samples After Treatment with Alkalies

Expt. No. and sample	4	8	10	11	12	13	14	15	16	17	18	19
Amino nitrogen (in %)	1.30	2.42	6.82	7.17	7.05	3.68	6.80	7.05	6.00	4.10	4.75	6.20

preliminary experiments that chitin swells but very little when treated with dilute sodium hydroxide solutions at −10 and −20° temperatures, since the chitin which separated after these treatments did not differ from the properties of the initial chitin (Table 2). By using a lower temperature, it was possible to put the chitin into solution (samples 10, 11, 12).

Thus in experiment No. 10, 125 ml of 8% sodium hydroxide solution was added to 5 g of chitin sifted through a 1 mm sieve. The flask was sealed with a cork and placed in the freezer, where −40° temperature was maintained, and after a given time interval freezing (20 minutes) was alternated with thawing at room temperature (1 hour). After 14 consecutive freezing and thawing operations, the authors succeeded in putting the chitin into solution. The solution was filtered through cheese cloth. If the solution was left a room temperature, then after a time lapse irreversible processes took place. After 2-4 weeks (depending upon the concentration of the solution), coagulation (precipitation) occurred, with gel formation, which did not break upon shaking. Upon storing the gel at room temperature, separation into two phases occurred — syneresis phenomenon.

The chitin solution obtained by alkali freezing, after filtering, was poured into a large volume of distilled water, whereupon chitin precipitated in highly dispersed form as large flakes. Washing was carried out with water and decantation. After removal of alkalies the chitin was separated on a filter, washed with methyl alcohol, acetone and ether. Drying was carried out in a vacuum desiccator without heating. Yield was 4.32 g (85.4% of chitin taken).

The preparation which separated, gray in color, was readily ground to a powder in a porcelain mortar, and dissolved in 2.25% acetic, 3% oxalic, dilute hydrochloric and sulfuric acids; swelled considerably in glacial acetic, formic and levulinic acids. It is necessary to note that this preparation did not swell after drying and did not dissolve in dilute alkalies at room temperature.

Experiments on freezing and thawing of alkalies with chitin are given in Table 2.

Analysis for acetyl content in the samples (as described by Brach) [16], indicated considerable decrease. Amino groups appearing instead were determined according to Van Slyke (Table 3).

From the data of Table 3, it can be seen that the amino nitrogen content in samples 4, 8, 13, 17 and 18 is negligible, while sample 18 content of amino nitrogen is higher than in other samples. This difference becomes understandable if one calculates the various alkali concentrations used in freezing. Moreover, it can be seen from the data of Table 3 that treatment of chitin with alkalies of various concentrations at −40° gave for the maximum amino nitrogen content for samples which dissolved or swelled greatly, with a sodium hydroxide concentration of 8 and 10%.

For samples 10 and 14 in 2.26% aqueous acetic acid, from viscosity-concentration curves, $\frac{\eta_{sp.}}{c}$ versus c (in g/100 ml), were found: $[\eta]$ 34.0 for sample 10 and $[\eta]$ 30.0 for sample 14, which considerably exceeded the characteristic viscosity values for chitin in 80.4% phosphoric acid. It is possible that deacetylated chitin is more readily soluble than chitin itself in organic and mineral acids, forming salts characterized by high viscosities.

For purposes of the reverse process of introducing acetyl groups into partially deacetylated chitin, acetylation of samples 10 and 16 with acetyl chloride was carried out in chloroform medium at room temperature for 14 days, and also with acetyl chloride for 3 hours, heating the acetyl chloride to boiling. With such treatment, however, there was no acetylation of the samples; the authors therefore used the procedure of acetylation with acetic anhydride in a sealed tube at 100° for 4 hours. As acetylation proceeded, a change in color of the initial samples was observed (from gray to a light yellow) as well as an increase in volume of the substance.

For sample 10 after acetylation there was found, according to analysis, the following (average of two determinations) in %: C 46.69; H 5.41; N 5.17; CH_3CO 20.20, which differed somewhat from analysis of the initial crab chitin (Table 1) in favor of oxygen enrichment and lowering of hydrogen and nitrogen contents; non-coincidence of numbers may be due to some hydrolysis of amino groups while treating with alkalies, which was not directly confirmed, however. Analysis for nitrogen was carried out according to Dumas and Kjeldahl.

Acetylated samples did not dissolve in, nor swell in, dilute organic acids; soluble in concentrated hydrochloric, 78-95% phosphoric, 60% sulfuric, 50.7% nitric acids, while dissolution was slower than for the initial chitin. Thus, with dissolution of chitin in 50.7% nitric acid, there was observed immediately after mixing a marked swelling and dissolution, whereas the samples treated with alkali in the cold and reacetylated, dissolved after a lapse of 18-20 hours. Apparently in the case given, greater or less density plays a role in gradual loosening of the substance.

The initial chitin had high porosity, while samples treated with alkali and then acetylated were in the form of a horny mass, and consequently solvent penetration was slower.

On the basis of experiments on chitin freezing in alkalies at various temperatures, it can be deduced that the maximum swelling of chitin proceeds at 8-10% sodium hydroxide and a temperature of −40°. Under such conditions dissolution of chitin in sodium hydroxide also proceeded in sodium hydroxide of the indicated concentrations. Moreover, hydrolytic rupture of the chitin acetyl groups proceeded and partially deacetylated chitin resulted.

Relation of Chitin to Phosphoric Acid

Determination of solubility of chitin in phosphoric acid was carried out at room temperature.

An weighed sample of absolutely dry chitin was stirred with the same amount of phosphoric acid in order to obtain a solution of concentration of 0.5 g in 100 ml. The acid was added dropwise from a buret. After addition of all acid, stirring was carried on periodically for 10-15 minutes. After 5 hours the suspension was filtered through a porous plate, and the residue washed on the filter with the same acid, then with water to a neutral reaction, and dried on the filter to constant weight at 105°.

The solubility was calculated in percentage of the content of absolutely dry chitin relative to initial batch. If the batch dissolved completely, which could be judged by a sample in the polarizing microscope, then the solution was not filtered and the solubility was marked as 100% (Fig 1).

Because of the fact that obtaining a concentrated solution of chitin in phosphoric acid is possible only under conditions of prolonged reaction, which may cause hydrolysis, the authors investigated the effect of time upon the properties of the solution in phosphoric acid and regenerated chitin (Table 4).

TABLE 4

Properties of chitin separated from solution immediately after storing. (80.4% acid, 4% chitin solution, temperature 17°)

Expt. No.	Dissolution time (in hours)	Additional heating	Copper number		Content of acetyl (in %)	
			Chitin		Chitin	
			of crayfish	of crab	of crayfish	of crab
1	6	–	1.22	2.84	20.16	20.00
2	5	1 hour at 40°	2.52	4.37	20.25	–
3	5	1 hour at 50°	6.10	7.65	–	20.10
4	24	–	4.34	4.57	–	–
5	48	–	5.68	5.52	–	–
6	72	–	7.20	7.50	20.15	20.00
7	96	–	8.75	8.54	–	–

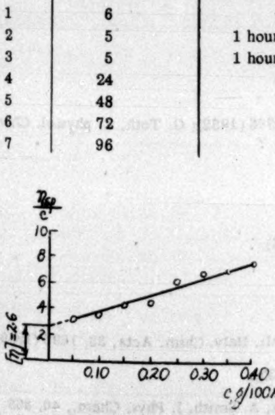

Fig. 2. Concentration curve for viscosity of chitin solution from crabs in 80.4% H_3PO_4.

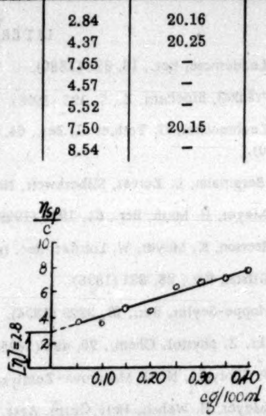

Fig. 3. Concentration curve of viscosity for crayfish chitin solutions in 80.4% H_3PO_4.

From concentrated solutions of chitin in phosphoric acid there can be prepared films 18-20 hours after dissolution, while at the same time films can be made from concentrated chitin solution in nitric acid 1 hour after dissolution. From the indicated concentrated solutions of chitin, the authors obtained layers which were intensely colored by wool dyes.

Dependence of solution viscosity on concentration for chitin of crayfish and of crab in 80.4% phosphoric acid was determined.

To determine this relationship, specific solutions were prepared of specific concentration by the weight method. The viscosity was determined in an Ostwald viscometer, 10 ml in volume. The viscometer was placed in a thermostat, where a constant temperature of 20° ± 0.01° was maintained.

On the basis of data experimentally obtained by the authors, curves were constructed for concentration ratio $\frac{\eta_{sp.}}{c} = f(c)$, extrapolation of which to zero concentration (Figs. 2,3) gave values for the intrinsic viscosity [2]. Thus it can be seen that the characteristic viscosities of crayfish and crab chitin are approximately the same, which may indicate the same length of macromolecule for crayfish and for crab chitin.

SUMMARY

1. It has been demonstrated that with repeated freezing of chitin in alkali and with subsequent thawing at room temperature, swelling proceeds, and even dissolution. Maximum swelling and dissolution results at 4% chitin concentration and 8 and 10% NaOH at a temperature of −40°.

2. Upon repeated freezing of chitin with subsequent thawing, there occurs a partial hydrolysis of acetyl groups, and their maximum hydrolysis corresponds to an NaOH concentration of 8 and 10%, and a temperature of −40°, i. e., maximum hydrolysis proceeds under the same conditions which produce considerable swelling and dissolution of chitin.

3. It has been established that 40, 45, 50 and 60% H_3PO_4 does not dissolve chitin, even upon prolonged reaction time, which contradicts literature data relative to the solubility of chitin in 45% phosphoric acid.

4. Complete dissolution of chitin proceeds at phosphoric acid concentrations in the range 78.40-97.20%. Higher concentrations of the acid are not convenient, since, on addition of chitin, there takes place crystallization of acid, and chitin does not swell.

Hydrolysis of chitin occurs over a period of time, as can be seen from increase in copper number of the samples.

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STUDY OF THE MOBILITY OF HYDROGEN ATOMS IN PHENAZOHYDRIN HYDROGEN BONDS

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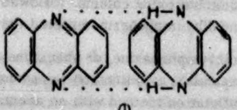
The phenazohydrins closely resemble the quinhydrones. The structure of these substances has not been clearly elucidated. The literature contains several variations for their structure [1], of which (I) seems probable, with the component molecules held by hydrogen bonds and situated in parallel planes.

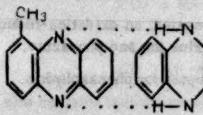


(I)

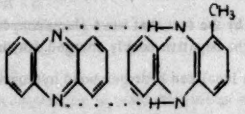
In our earlier work [2] in which benzoquinhydrone was studied by the isotope method, it was shown that the hydrogen in the hydrogen bonds in this substance is localized at the hydroquinone nucleus and can only be displaced to the other nucleus on heating with an activation energy of about 32 kcal/mol.

In the present study the isotope method was used for the solution of analogous problems of phenazohydrin structure, and for this purpose, as in the work with quinhydrone, phenazohydrin was prepared from heavy phenazine and ordinary dihydrophenazine and then separated into its components. Although the conditions for the preparation and separation of this substance were close to those used in the work with quinhydrone, the opposite result was obtained: the deuterium was equally divided between the phenazine and the dihydrophenazine, which appears to indicate that the nuclei of these substances in the phenazohydrin molecule are equivalent.

Analogous results were previously obtained by Clemo and McIlwain [1]. They showed that the phenazohydrins, which should have the structures (II) and (III) according to their method of preparation, are identical.

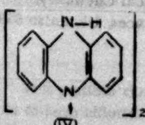


(II)



(III)

However, our results and those of Clemo and McIlwain cannot be considered as proof of the equivalence of the component nuclei in phenazohydrin, as they have another explanation, and furthermore both the possible variants of structure with equivalent nuclei are unsatisfactory. The Structure (IV) does not explain the very easy dissociation of phenazohydrin into its components in solution. Structure (I) with a delocalized hydrogen bond hydrogen is improbable, as phenazohydrin should be analogous to benzoquinhydrone with regard to hydrogen mobility in the hydrogen bonds. Indeed, in its molecule hydrogen can be displaced only as a neutral atom and with the same bond rearrangement as in benzoquinhydrone. As regards the mobility of the hydrogen, the great N–N distance and the low energy of the hydrogen bond with nitrogen, with a high value for the energy of the N–H bond, suggest that the potential barrier for hydrogen displacement in phenazohydrin is high, and is not lower than in benzoquinhydrone. On the basis of these considerations and the chemical behavior we believe that phenazohydrin has Structure (I), with the hydrogen atoms localized at the dihydrophenazine nucleus.



(IV)

The most natural explanation of the results of this work is that during preparation of phenazohydrin an oxidation-reduction equilibrium is set up in the solution between the doubly charged negative dihydrophenazine ion and phenazine, similarly to the well-known effect in quinhydrones. Another possible explanation presupposes the formation in the solution of small concentrations of radicals of the same type (IV in monomer form) from both components, leading to equal distribution of deuterium between the nuclei. Clemo and McIlwain's results afe explained similarly.

Heavy phenazine* was prepared by heating phenazine with D_2O in the presence of a small amount of sulfuric acid for 48 hours at 185°. No exchange takes place in the same conditions but in the presence of alkali.

Heavy phenazohydrin was prepared by two methods: by evaporation of an ether solution of equimolar amounts of the components in a stream of CO_2, or by mixing saturated dioxane solutions of the components at room temperature.

The resolution into the components was effected in two ways. a) 0.09 g of heavy phenazohydrin was heated to 96° at 10^{-4} mm in the previously described quartz apparatus 20 mm in diameter, when the phenazine sublimed on the cold walls while the dihydrophenazine remained in the lower part of the apparatus. The resolution was completed in 1.5 hours. The melting point of the phenazine was 174-174.5°, and that of the dihydrophenazine 210.7°. The yield was almost quantitative. b) An ether solution of equimolar amounts of heavy phenazine and dihydrophenazine was passed in a stream of nitrogen through an aluminum oxide column, followed by washing with ether, when first phenazine and then a mixture of phenazohydrin and dihydrophenazine entered the receiver.

Isotope analysis. The phenazine and dihydrophenazine, or phenazine and the mixture of phenazohydrin and dihydrophenazine (in the chromatographic separation experiments) were burnt, and the water after the combustion was analyzed for deuterium content by the microflotation method with an accuracy of ± 3%.

It was found that, regardless of the method used for the preparation and separation of the phenazohydrin, the deuterium contents of its components were the same within the limits of experimental error: they were from 47 to 49% of the original amount of deuterium in the phenazine, and from 48 to 49.5% in the dihydrophenazine.

During the development of the chromatographic separation method it was found that heavy benzoquinhydrone can also be separated by this method; the quinone and quinhydrone obtained contain equal amounts of deuterium. A control experiment showed that when an ether solution of quinhydrone was kept 5 hours at room temperature, followed by separation by means of vacuum distillation, the deuterium contents in the quinone and hydroquinone were not equal. The catalytic effect of aluminum oxide on the transfer of hydrogen in quinhydrone is analogous to the effect of glass which was previously observed by us.

SUMMARY

1. It was found that phenazohydrin prepared from heavy phenazine and ordinary dihydrophenazine yields phenazine and dihydrophenazine with equal deuterium contents when resolved into its components.

2. This is explained by the fact that when phenazohydrin is prepared, an oxidation-reduction equilibrium is set up in solution between the negative doubly charged dihydrophenazine ion and phenazine.

3. Structure (I), with localized hydrogen bond hydrogen, is adopted for phenazohydrin.

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* The experiments were performed with the assistance of T. G. Lando and Yu. Ya. Fialkov.

** T. p. = C. B. Translation pagination.

PHOTOLYSIS OF PENTACHLOROETHANE

G. A. Razuvaev and N. A. Osanova

In an investigation of photochemical reactions in solutions of polyhalogenated compounds we observed the decomposition of pentachloroethane which proceeds with evolution of hydrogen chloride. It was first presumed that the formation of perchloroethylene according to the following Scheme is possible in this reaction:

$$C_2HCl_5 \xrightarrow{h\nu} Cl\cdot + C_2HCl_4\cdot, \qquad (1)$$

$$C_2HCl_5 + Cl\cdot \rightarrow HCl + C_2Cl_5\cdot, \qquad (2)$$

$$C_2Cl_5\cdot \rightarrow Cl\cdot + C_2Cl_4. \qquad (3)$$

In reality the process is much more complicated, as we were able to obtain from the reaction products a number of chlorine derivatives of butane, namely: heptachlorobutane, octachlorobutane, nonachlorobutane, decachlorobutane, and also hexachloroethane. A more detailed investigation of this reaction was therefore of interest. By analogy with the thoroughly studied reactions of the decomposition of carbon tetrachloride [1], the photolysis of pentachloroethane is undoubtedly a radical mechanism reaction which proceeds with the removal of chlorine and the formation of the tetrachloroethyl radical (I). From this, chlorinated butanes may be obtained either by dimerization of the radicals formed, or by the addition of polyhalogenated ethane derivatives to unsaturated compounds [1]. The formation of unsaturated compounds is possible as the result of the decomposition of chlorinated ethyl radicals (3), which is confirmed by a number of studies. For example, in the thermal decomposition of hexachloroethane chlorine is split off and the pentachlorethyl radical is formed:

$$C_2Cl_6 \rightarrow C_2Cl_5\cdot + Cl,$$

which then decomposes to form perchloroethylene.

Perchloroethylene is formed in free radical reactions of saturated hydrocarbon chlorination [2], initiated by tertiary butyryl or benzoyl peroxides, according to the Scheme:

$$R'-O-OR' \rightarrow 2R'O\cdot,$$

$$R'O\cdot + RH \rightarrow R'OH + R\cdot,$$

$$R\cdot + C_2Cl_6 \rightarrow RCl + C_2Cl_5\cdot,$$

$$C_2Cl_5\cdot \rightarrow Cl\cdot + C_2Cl_4,$$

$$Cl\cdot + RH \rightarrow HCl + R\cdot.$$

The literature also contains indications of the decomposition of other chlorinated ethyl radicals. For example, in the pyrolysis of 1,1,1-trichloroethane [3], the trichloroethyl radical formed decomposes with the formation of vinylidene chloride:

$$CCl_3CH_3 \rightarrow CCl_3\cdot + CH_3\cdot,$$

$$CCl_3CH_3 + CCl_3\cdot \rightarrow CCl_3CH_2\cdot + CHCl_3,$$

$$CCl_3CH_2\cdot \rightarrow Cl\cdot + CCl_2{=}CH_2.$$

The thermal decomposition of tetrachloroethanes proceeds with the formation of trichloroethylene [4] owing to decomposition of the tetrachloroethyl radical:

$$C_2H_2Cl_4 + Cl\cdot \rightarrow HCl + C_2HCl_4\cdot,$$

$$C_2HCl_4\cdot \rightarrow CCl_2{=}CHCl + Cl\cdot.$$

It is possible that the unsaturated compounds formed in the photolysis of pentachloroethane can add on to the latter to form chlorinated butane derivatives

$$C_2Cl_4 + C_2HCl_5 \rightarrow C_4HCl_9.$$

On the other hand, as was already pointed out, the chlorinated ethyl radicals (1) and (2) may dimerize to form octachlorobutane, decachlorobutane, and also nonachlorobutane:

$$2C_2HCl_4\cdot \rightarrow C_4H_2Cl_8,$$
$$2C_2Cl_5\cdot \rightarrow C_4Cl_{10},$$
$$C_2HCl_4\cdot + C_2Cl_5\cdot \rightarrow C_4HCl_9.$$

The literature contains numerous references [1] to the possible dimerization of the CCl_3 radical and also of the CH_2Cl radical obtained in the decomposition of CH_3Cl photosensitized by mercury [5]. The dimerization of radicals of the ethane series has also been reported. For example, dichloroethyl and tetrachloroethyl radicals are dimerized to form tetrachlorobutane and octachlorobutane in the thermal reaction of benzoyl peroxide with 1,2-dichloroethane and 1,1,2,2-tetrachloroethane [6]:

$$2CH_2Cl-\dot{C}HCl \rightarrow CH_2Cl-CHCl-CHCl-CH_2Cl,$$
$$2CHCl_2-\dot{C}Cl_2 \rightarrow CHCl_2-CCl_2-CCl_2-CHCl_2.$$

Numerous instances of radical dimerization have also been observed in the thermal reaction of acetyl peroxide with various types of substituted hydrocarbons of the methane and ethane series [7]. In the photolysis of pentachloroethane radical dimerization is more probable, as the decomposition of chlorinated ethane radicals usually occurs at higher temperatures. From the reaction products it may be supposed that two processes occur in the reaction:

1) dimerization of the tetrachloroethyl radicals initially formed according to Equation (1), with the formation of octachlorobutane:

$$2C_2HCl_4\cdot \rightarrow C_4H_2Cl_8;$$

2) the chlorination, by the chlorine formed, both of the original pentachloroethane to form hexachloroethane, and of the dimerization product of octachlorobutane to form nonachlorobutane and decachlorobutane

$$C_2HCl_5 \xrightarrow{Cl} C_2Cl_6,$$
$$C_4H_2Cl_8 \xrightarrow{Cl} C_4HCl_9 \xrightarrow{Cl} C_4Cl_{10}.$$

The formation of decachlorobutane could also be attributed to dimerization of pentachloroethyl radicals, but more probably it is formed according to the above chlorination reaction. The latter is also confirmed by the following: in experiments with comparatively short irradiation times the amount of octachlorobutane was relatively greater, while upon prolonged irradiation the amount of octachlorobutane decreased and that of nonachlorobutane and decachlorobutane increased. The formation of heptachlorobutene could be explained by the removal of the elements of hydrogen chloride from octachlorobutane during vacuum distillation of the reaction mixture.

The formation of tarry matter indicates that the photolysis of pentachloroethane is also accompanied by a number of other side reactions.

EXPERIMENTAL

Synthesis of pentachloroethane. Pentachloroethane was prepared by chlorination of trichloroethylene under irradiation. The reaction product was washed with weak solutions of soda, sulfite, and water; it was dried over calcium chloride and fractionated. The fraction with b.p. 159-162° and n_D^{20} 1.5030 was collected. Literature data: b. p. 162° n_D^{15} 1.5054 [9].

Photolysis of pentachloroethane. Pentachloroethane was irradiated in quartz test tubes, 20 mm diameter, by ultraviolet light from a PRK-2 lamp for a long time (from 250 to 500 hours) at a distance of 200 mm from the lamp. The irradiation was accompanied by evolution of hydrogen chloride, which was absorbed by solid alkali contained in traps specially attached to the stoppers of the tubes. It was necessary to change the alkali from time to time. The combined photolysis product from several tubes was washed with weak soda solution to remove hydrogen chloride and then with water, dried over calcium chloride, and distilled in vacuum: the unreacted pentachloroethane distilled at 65-75° and 75-80 mm. The last pentachloroethane fractions contained hexachloroethane, which was obtained pure by a repeated distillation of the pentachloroethane over a large plate-type distillation column. The oily liquid which remained after removal of the pentachloroethane was distilled under vacuum. The evolution of hydrogen chloride and formation of tarry matter was observed in the process. Preliminary analysis of the distilled liquid showed that it was a mixture of chlorinated derivatives of the butane series. The mixture obtained in a large number of experiments was repeatedly fractionated under vacuum in order to separate it into its components. The following were isolated in the separation:

1) Heptachlorobutene, b.p. 110-120° at 5 mm, n_D^{20} 1.5529. Literature data [8]: b.p. 210° at 760 mm, n_D^{20} 1.5529.

Found %: Cl 83.59, 83.14, 83.38; M 286.59, 287.65, 285.37. C_4HCl_7. Calculated %: Cl 83.50; M 297.3.

The reaction of heptachlorobutene with alcoholic alkali yielded hexachlorobutadiene: 2.23 g of the substance was dissolved in ethyl alcohol, the solution was cooled, and a cooled 0.1 N alcoholic KOH solution was added with phenolphthalein indicator. The product after removal of the hydrogen chloride was precipitated by water, dried over calcium chloride, and distilled under vacuum. The yield was 0.6 g of a substance with b.p. 210° at 760 mm (by Sivolobov's micro method) n_D^{20} 1.5532. Literature data [8,9]: b.p. 210° at 760 mm, n_D^{20} 1.5531.

Found %: Cl 82.04, 82.19; M 260.73. C_4Cl_6. Calculated %: Cl 81.58; M 260.8.

2) Octachlorobutane, white rhombic crystals, m.p. 78° (from ethyl alcohol). Literature data [10]: m.p. 75-76°.

Found %: Cl 85.01, 84.80, 84.50; M 318.63, 315.38, 319.62. $C_4H_2Cl_8$. Calculated %: Cl 85.03; M 333.7.

3) Nonachlorobutane, b.p. 150-160° at 5 mm, n_D^{20} 1.5798. Literature data [8]: n_D^{20} 1.5798, b.p. 123° at 0.1 mm.

Found %: C 13.20, 12.93; H 0.31, 0.30; Cl 86.45, 86.28; M 354.26, 362.49, 360.0. C_4HCl_9. Calculated %: C 13.05; H 0.27; Cl 86.68; M 368.2.

The action of alcoholic alkali on nonachlorobutane yielded octachlorobutene. 12.14 g of the substance was treated with alcoholic KOH solution as previously. 5 g of a substance with b.p. 125-130° at 6 mm, and n_D^{20} 1.5784, was distilled under vacuum. Literature data [8]: b.p. 97° at 0.1 mm, n_D^{20} 1.5789.

Found %: Cl 84.91. 85.17; M 319.75, 317.62, 324.48. C_4Cl_8. Calculated %: Cl 85.53; M 331.7.

4) Decachlorobutane, white crystals, had m.p. 98° after repeated recrystallization from methyl alcohol. Literature data [8]: m.p. 101°.

Found %: Cl 88.05, 88.00, 88.13; M 383.13, 390.34, 382.61. C_4Cl_{10}. Calculated %: Cl 88.07; M 402.6.

5) Hexachloroethane, m.p. 185° sublimed over concentrated H_2SO_4, and gave no melting point depression with the pure substance. Literature data: m.p. 186.9 - 187.4° [11].

In the course of a series of experiments it was observed that the amount of decachlorobutane formed increased, and that of octachlorobutane decreased, with increase irradiation time. In some instances octachlorobutane was not isolated in solid form after prolonged exposure. As an example we give the results of one of the experiments carried out with prolonged irradiation (500 hours). The 500 g of pentachloroethane taken, after removal of the unreacted compound, yielded 17 g of hexachloroethane and 50.5 g of an oily product, from which 39 g of a mixture of polyhalogenated butane derivatives and 9 g of resin was obtained by distillation. The following fractions were obtained by vacuum distillation of the polyhalogenated mixture: first, b.p. 100-125° at 5 mm, 6.5 g, which was heptachlorobutene; second, b.p. 127-145° at 5 mm, 5.5 g, a mixture of 70% heptachlorobutene and 30% octachlorobutane, as confirmed by analyses of this fraction and conversion of it into hexachlorobutadiene by the action of alcoholic alkali.

Found %: Cl 84.01, 83.87, 83.79; M 323.48, 325.09, 322.86. Calculated octachlorobutane content: 28.75.

4.26 g of substance after treatment with alcoholic alkali: 2.5584 g AgCl. Calculated octachlorobutane content: 31.39%.

The third fraction, b.p. 148-160° at 5 mm, 24.4 g, was a mixture of 66.6% nonachlorobutane and 33.4% decachlorobutane. To isolate the latter, the fraction was treated with alcoholic alkali. This converted nonachlorobutane into octachlorobutene, which was distilled off to leave 8.17 g solid decachlorobutane. Thus, the nonachlorobutane content was 16.23 g. The residue after distillation of the polyhalogenated mixture (39 g) was 2.6 g of resin.

SUMMARY

1. It is shown that when pentachloroethane is irradiated by ultraviolet light hydrogen chloride is evolved and chlorinated butane derivatives are formed: octachlorobutane, nonachlorobutane, decachlorobutane, and also hexachloroethane.

2. A reaction scheme is proposed: the primary process is removal of a chlorine atom from pentachloroethane with the formation of tetrachloroethyl radicals, which dimerize to octachlorobutane. The chlorine evolved chlorinates both the original pentachloroethane, and the octachlorobutane formed, to yield nona- and decachlorobutane.

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FREE RADICAL REACTIONS IN SOLUTIONS

II. RELATIVE ACTIVITY OF FREE RADICALS IN REACTIONS WITH ISOPROPYLBENZENE, CYCLOHEXENE AND POLYMERS

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The activity of free radicals in their interaction with solvents (LH) is usually characterized by the extent to which the following reaction proceeds:

$$R\cdot + LH \rightarrow RH + L\cdot . \qquad (1)$$

From the yield of the product RH it is at the same time possible to evaluate the mobility of the H atoms of the solvent reacting with the free radicals. This criterion was used in a number of investigations, including studies of the decomposition of metalorganic compounds in various media [1, 2], in the electrolysis of Grignard reagents [3], in studies of the photolysis products of aliphatic ketones [4], and in the pyrolysis of peroxides [5]. A strict generalization of the experimental data obtained in these studies is not possible because of the very diverse experimental conditions used. In the present study data on the relative activities of a number of free radicals, which differ considerably from each other in reactivity, were obtained on the basis of a study of the thermal decomposition products of diazoaminocompounds in solution. The decomposition, which proceeded according to the Equation

$$R{-}N{=}N{-}NH{-}Ar \rightarrow R\cdot + N_2 + \cdot NH{-}Ar, \qquad (2)$$

took place under temperature conditions which ensured comparable decomposition rates of the diazoamino compounds, which were used in molar concentrations of 1.2-1.3%. In addition to determination of the yields of the products RH, a full study of the final reaction mixtures was made for many of the original compounds, and the yields of products obtained by other reactions, in particular:

$$2R\cdot \rightarrow R + R, \qquad (3)$$

$$R\cdot + \cdot NH{-}Ar \rightarrow R{-}NH{-}Ar, \qquad (4)$$

$$2L\cdot \rightarrow L{-}L, \qquad (5)$$

were determined.

The main results of the investigation are given in Tables 1 and 2, which also include data obtained in a study of the decomposition products of azoisobutyronitrile.

In addition to the compounds formed according to Reactions (1), (3), (4), and (5), the triazene decomposition products contain about 30% of aniline [or diphenylamine in the case of di(diphenyl) triazene].

Most probably only a small part of it is formed by the reaction

$$C_6H_5NH\cdot + LH \rightarrow C_6H_5NH_2 + L\cdot , \qquad (6)$$

as there are no reasons for supposing that the activity of the anilino radical is so high. Indirect evidence of the low activity of the $C_6H_5NH\cdot$ radical is its inability to bring about vulcanization, as will be shown below. The fact that Reaction (6) nevertheless occurs is confirmed by the formation of the L-L product (dicumyl and dicyclohexenyl) in the decomposition of allyl- and benzylphenyltriazenes, that is, in cases when there is practically no removal of H atoms from isopropylbenzene by the free hydrocarbon radicals.

The free radical disproportionation reaction of the type

$$2C_nH_{2n+1}\cdot \rightarrow C_nH_{2n} + C_nH_{2n+2} \qquad (7)$$

proceeds to a slight extent in the experimental condition used (Table 3).

The total absence of aliphatic amines in the alkyl aryl triazene decomposition products indicates that of the two possible structures

TABLE 1

Conversion Products of Free Radicals in Isopropylbenzene

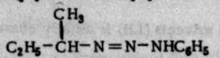
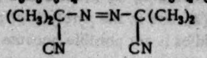
Original Compound		Temp. of Exp.	Yield (in %)			
Name	Formula		RH	R−R	R−NHAr	L−L
Methylphenyltriazene	$CH_3N=N-NHC_6H_5$	120*	56	0	26	17
Ethylphenyltriazene	$C_2H_5N=N-NHC_6H_5$	120	30	0	−	−
n-Propylphenyltriazene	$C_3H_7N=N-NHC_6H_5$	120	20	0	25	6
Isopropylphenyltriazene	$(CH_3)_2CHN=N-NHC_6H_5$	120	9	0	25	3
n-Butylphenyltriazene	$C_4H_9N=N-NHC_6H_5$	120	10	12	29	8
sec-Butylphenyltriazene	 $C_2H_5-\overset{CH_3}{\overset{\vert}{C}}H-N=N-NHC_6H_5$	120	6	−	−	−
tert-Butylphenyltriazene	$(CH_3)_3CN=N-NHC_6H_5$	110	0	0	30	−
Allylphenyltriazene	$C_3H_5N=N-NHC_6H_5$	120	0.2	13	34	3
Crotylphenyltriazene	$C_4H_7N=N-NHC_6H_5$	100	0	−	35	−
Benzylphenyltriazene	$C_6H_5CH_2N=N-NHC_6H_5$	120	0	25	29	3
di(Diphenyl)triazene	$C_6H_5C_6H_4N=N-NHC_6H_4C_6H_5$	140	46	5	−	9
Azoisobutyronitrile	 $(CH_3)_2\underset{\underset{CN}{\vert}}{C}-N=N-\underset{\underset{CN}{\vert}}{C}(CH_3)_2$	80	10	82	−	6

TABLE 2

Conversion Products of Free Radicals in Cyclohexene. (Decomposition Temperature 120°)

k·	Yield (in %)					
	RH	R−R	$R-NHC_6H_5$	L−L *	L−R	$L-NHC_6H_5$
$CH_3\cdot$	61	0	17	51	0	6
$C_6H_5CH_2\cdot$	0	20	34	24	6	0
$(CH_3)_2\cdot C-CN$	16	65	−	0	12	−
$C_2H_5\cdot$	45	Reaction mixtures not studied				
$n-C_3H_7\cdot$	29					
$n-C_4H_9\cdot$	5					
$CH_2=CH-CH_2\cdot$	2					

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* The methylphenyltriazene decomposition products also contained tercyclohexenyl (L−L−L) in 6% yield.

$$\underset{(I)}{R-N=N-NHC_6H_5} \text{ and } \underset{(II)}{RNH-N=N-C_6H_5}$$

only Structure (I) exists, at least at the time of decomposition.

It must be pointed out that Razuvaev, Fedotova, and Ovchinnikova, who studied the decomposition products of benzylphenyltriazene in carbon tetrachloride and ethylene glycol monoethyl ether [6], reached somewhat different conclusions on the decomposition mechanism of triazenes. It is possible that the specific peculiarities noted in the paper cited are due to the experimental conditions, which differed considerably from ours (in particular, the use of polar solvents and the presence of mercury).

From the results shown in Tables 1 and 2 it follows that Reaction (I) proceeds to a greater extent in the case of cyclohexene, which accounts for the increased yields and numbers of conversion products of the solvent radicals L·. No products of the addition of free radicals to the cyclohexene double bonds were isolated in any instance. This indicates the much lower reactivity of internal double bonds in comparison with α-methylene groups, in agreement with literature data [7].

In the case of hydrazobenzene it was shown that when the reaction medium used is a compound with particularly mobile hydrogen atoms, the Reaction (I) may be brought about even for such free radicals as allyl and crotyl (Table 4).

TABLE 3

Extent of the Disproportionation Reaction of Alkyl Free Radicals in Isopropylbenzene Solution*

C_nH_{m+1}	Yield of C_nH_m (in %)
$C_2H_5\cdot$	1
n-$C_3H_7\cdot$	1
iso-$C_3H_7\cdot$	3
n-$C_4H_9\cdot$	1
sec-$C_4H_9\cdot$	1
tert-$C_4H_9\cdot$	6

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* The data on the yields of the products RH (Tables 1 and 2) are given with a correction by the subtraction of the amount of RH formed by Reaction 7.

TABLE 5

Yields of RH Products in Benzene Solutions of Rubbers at 120°

Radical	Yield of RH (in %)		
	in benzene	in natural rubber solution	in polybutadiene solution containing about 50% of 1, 2 links
$CH_3\cdot$	12	27	19
$C_2H_5\cdot$	8	18	10
n-$C_3H_7\cdot$	6	15	9
n-$C_4H_9\cdot$	0	5	5
$CH_2=CH-CH_2\cdot$	0	0.3	0.5

TABLE 4

Yields of RH Products of the Thermal Decomposition of Triazene in Hydrazobenzene at 131°

R·	RH (in %)
$CH_3\cdot$	65
$CH_2=CH-CH_2\cdot$	8
$CH_3-CH=CH-CH_2\cdot$	6

In view of the fact that Reaction (I) is one of the causes of branching under polymerization conditions, it appeared of interest to determine the activity of free radicals in this reaction in relation to polymer molecules. For this purpose a study was made of the gaseous products formed in the decomposition of triazenes in benzene solutions of polyisoprene and polybutadiene (Table 5).

The formation of RH products during the decomposition of some triazenes in pure benzene is most likely caused by interaction between free radicals and triazene decomposition products, as, according to the literature [2], the possibility of Reaction (1) occurring in the case of benzene is doubtful.

The vulcanizing power of triazenes was chosen as another criterion of the relative activities of free radicals toward polymers, since the initial stages which lead to vulcanization are associated with reactions of the type

$$R\cdot + \sim CH_2-CH=CH-CH_2\sim \;\rightarrow\; RH + \sim CH-CH=CH-CH_2\sim. \qquad (8)$$

$$R\cdot + \sim CH_2-CH=CH-CH_2\sim \;\rightarrow\; \sim CH_2-CHR-CH-CH_2\sim. \qquad (9)$$

TABLE 6

Yield of Gel Fraction in the Bulk Vulcanization of Natural Rubber at 120° (Amount of Initiator was Equivalent to 5% by Weight of Benzoyl Peroxide)

Initiator	Heating time (min)	Yield of gel fraction (in %)
Di(diphenyl)triazene	5	0
	10	65
	20	76
	60	90
Diazoaminobenzene	5	0
	10	21
	30	65
	60	84
Methylphenyltriazene	120	13
	240	44
	360	48
Isopropylbenzene hydroperoxide	40	8
	60	18
	120	28
	240	68
Benzoyl peroxide	2	11
	5	60
Allylphenyltriazene	300	0
Benzylphenyltriazene	300	0

The vulcanizing action was measured by the degree of formation of the insoluble form (gel fraction) when natural rubber was heated with various sources of free radicals (Table 6). For comparison, this Table also contains data on the vulcanizing action of benzoyl peroxide and isopropylbenzene hydroperoxide.

The absence of gel fraction in the decomposition of allyl- and benzylphenyltriazenes in the bulk of the rubber also indicates the low activity of the anilino radical formed during the decomposition of triazenes (Reaction 2).

In accordance with the above results, the relative free radical activities in the hydrogen atom removal reaction may be expressed by the following series:

$$CH_3\cdot > C_6H_5{-}C_6H_4\cdot > C_2H_5\cdot > n\text{-}C_3H_7\cdot > n\text{-}C_4H_9\cdot \geqslant$$
$$\geqslant (CH_3)_2\dot{C}{-}CN > iso\text{-}C_3H_7\cdot > sec.\text{-}C_4H_9\cdot > CH_2{=}CH{-}CH_2\cdot >$$
$$> CH_2{-}CH{=}CH{-}CH_2\cdot,\ C_6H_5CH_2\cdot,\ (CH_3)_3C\cdot.$$

EXPERIMENTAL

Synthesis of triazenes. Methyl-, n-butyl-, allyl-, and benzylphenyltriazenes were prepared by the action of phenyldiazonium chloride on the corresponding amines [8]. Di(diphenyl)triazene was synthesized by the passage of carbon dioxide through an alcohol solution of p-aminodiphenyl containing potassium chromate and sodium nitrite [9]. All the other triazenes were prepared by the action of the corresponding alkylmagnesium bromides on phenyl azide [10]. Only data on triazenes synthesized for the first time are given below.

Propylphenyltriazene. Colorless crystals:

m.p. 16.5-18°, d_4^{20} 1.0125, n_D^{20} 1.5810.
Found %: C 66.05, 65.70; H 8.06, 7.93; N 25.82, 26.10. M 162, 165. $C_9H_{13}N_3$. Calculated %: C 66.25; H 7.97; N 25.76. M 163.

Isopropylphenyltriazene. Pale yellow oil:

d_4^{20} 1.0073, n_D^{20} 1.5750.
Found %: C 65.90, 65.50; H 7.93, 7.87; N 25.86, 25.88. M 162.5, 162. $C_9H_{13}N_3$. Calculated %: C 66.25, H 7.97; N 25.76. M 163.

n-Butylphenyltriazene. Colorless crystals:

m.p. 17-18°, d_4^{20} 0.9921, n_D^{20} 1.5690.
Found %: N 23.40, 23.00. M 174, 178. $C_{10}H_{15}N_3$. Calculated %: N 13.67. M 177.

The silver derivative forms bright yellow crystals, m.p. 101-102°.

sec-Butylphenyltriazene. This was not isolated pure. The crude product was a dark oil which contained, according to the amount of nitrogen evolved on pyrolysis, 54% of the triazene.

tert-Butylphenyltriazene. Dark brown oil. The silver derivative forms pale yellow crystals, m.p. 149°.

Found %: Ag. 37.65. $C_{10}H_{14}N_3Ag$. Calculated %: Ag 38.00.

Allylphenyltriazene. Colorless crystals:

m.p. 8-10°, d_4^{20} 1.0070, n_D^{20} 1.5551.
Found %: N 25.75, 25.69. M 164, 164. $C_9H_{11}N_3$. Calculated %: N 26.04. M 161.

The silver derivative forms pale yellow crystals, m.p. 132° (decomp.).

Crotylphenyltriazene. This was not isolated pure. The crude product was a dark oil which contained, according to the amount of nitrogen evolved on pyrolysis, 80% of the triazene.

Di(diphenyl)triazene. Pale yellow needles: m.p. 147.5-148°.

Found %: N 12.22, 11.70. M 343, 340. $C_{24}H_{19}N_3$. Calculated %: N 12.02. M 349.

Investigation of the decomposition products. The original compounds were decomposed in ampoules connected to gas burets by long necks. The ampoule necks were provided with cooling jackets. In the cases of cyclohexene and benzene the decomposition was carried out under 750-800 mm excess pressure, which was regulated by means of an open mercury manometer connected to the system. The decomposition was continued till gas evolution ceased, which usually required 5-6 hours. The gaseous products were analyzed with the aid of the VTI gas analyzer. A metal cap column was used for the distillation of the reaction mixture. The residue after removal of the main bulk of solvent was treated with hydrochloric acid to separate the amines. The primary and secondary amines were separated with the aid of metaphosphoric acid [11]. The hydrocarbon portion was distilled over a metal cap microcolumn. The experiments were performed in duplicate, and mean values are given in the tables. Results of several typical experiments are given below.

1st Experiment. 6 g of methylphenyltriazene was decomposed in 500 ml of isopropylbenzene. 1510 ml * of gas was evolved. The composition of the gas was: methane 36% (yield 55%), nitrogen 64% (yield 97.5%). The following products were isolated from the reaction mixture: a) aniline, 1.35 g (yield 33%), hydrochloride m.p. 194° (mixed sample 193°); b) methylaniline, 1.20 g (yield 25%), hydrochloride m.p. 123° (mixed sample 123°); c) 2,3-dimethyl-2,3-diphenylbutane (dicumyl), 1.8 g (yield 17%), m.p. 119-120° (from methyl alcohol), literature data: m.p. 120° [12].

Found %: M 215, 221. $C_{18}H_{22}$. Calculated M 238.

2nd Experiment. 13.5 g of methylphenyltriazene was decomposed in 900 ml of cyclohexene. 3620 ml of gas was evolved. The composition of the gas was: methane 38.4% (yield 61.3%), nitrogen 61.6% (yield 98.5%). The following products were isolated from the reaction mixture: a) aniline, 5.0 g (yield 54%); b) methylaniline, 1.8 g (yield 17%; c) cyclohexenylamine, 1.0 g (yield 6.0%): b.p. 140-143° at 3 mm.

Found %: N 8.04. M 182, 186; number of double bonds, 1.01.** $C_{12}H_{17}N$. Calculated %: N 8.00. M 175. Number of double bonds, 1.

d) Dicyclohexenyl, 8.2 g (yield 50%):

B.p. 80.5-81.5 at 4 mm, d_4^{20} 0.9310, n_D^{20} 1.5100, MR_D 52.25. $C_{12}H_{18}\overline{|}_2$. Calc. 52.28.
Found: M 159, 159; number of double bonds 2.02, 2.00. $C_{12}H_{18}$. Calculated: M 162. Number of double bonds 2.

e) Tercyclohexenyl, 1.0 (yield in %):

B.p. 140-141° at 4 mm, d_4^{24} 0.9930, n_D^{24} 1.5380, MR_D 76.8. $C_{18}H_{28}\overset{=}{}_3$. Calc. 77.3.
Found: M 222, 216; number of double bonds 3.03. $C_{18}H_{28}$. Calculated: M 242. Number of double bonds 3.

3rd Experiment. 12 g of benzylphenyltriazene was decomposed in 450 ml of cyclohexene. 1060 ml of gas was evolved. The gas was pure nitrogen (yield 83.0%). The following products were isolated from the reaction mixture: a) aniline, 2.3 g (yield 44%); b) benzylaniline, 3.7 g (yield 35%), hydrochloride m.p. 209-210°.

Found %: N 7.45, 7.60. M 182, 179. $C_{13}H_{13}N$. Calculated %: N 7.65. M 183.

c) Dicyclohexenyl 2.35 g (yield 26%), b.p. 242-245°.

Found: M 161, 158; number of double bonds 1.98. $C_{12}H_{18}$. Calculated: M 162; number of double bonds 2.

d) Dibenzyl, 1.0 g (yield 19%), m.p. 47-48°, mixed sample 47°.

4th Experiment. The decomposition of triazenes in benzene solutions of rubbers was carried out at 120° in all cases, with concentrations: rubber, 3.5% by weight, triazene, 0.66 molar %. The rubber samples were previously extracted with acetone in a Soxhlet apparatus for 4 hours. 1 g of methylphenyltriazene was decomposed in 130 ml of benzene containing 4 g of natural rubber. 205 ml of gas was evolved. The composition of the gas was: nitrogen 77.9% (yield 98.5%), methane 22.1% (yield 27.3%).

Evaluation of vulcanizing power. The compound under investigation was masticated on cold rolls for 5 minutes with a definite amount of natural rubber. Separate 0.7-1.0 g portions of the "hide" formed were heated in nitrogen in sealed ampoules at 120° for different times. A weighed sample of the ampoule contents (~ 0.35 g) was then extracted with chloroform in a Soxhlet apparatus for 15 hours, after which the weight of the undissolved residue was determined.

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* The gas volume is reduced to standard conditions.

** The degree of unsaturation (number of double bonds) was in all cases determined by hydrogenation in ethyl alcohol solution over Pd black.

SUMMARY

1. Propylphenyltriazene, isopropylphenyltriazene, butylphenyltriazene, tert-butylphenyltriazene, allylphenyltriazene, and di(diphenyl)triazene were prepared and described for the first time.

2. The thermal decomposition products of a number of triazenes in isopropylbenzene, cyclohexene, and benzene solutions of rubber were studied.

3. The order of the activities of free radicals in the reaction of H atom removal from various compounds has been established. It was shown that the allyl, crotyl, benzyl, and tert-butyl free radicals practically do not react with isopropylbenzene.

4. It was established that free radicals of low activity (allyl, benzyl, and anilino) do not induce structurization of natural rubber.

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MECHANISM OF THE CATALYTIC ACTION OF ALUMINUM CHLORIDE

IV. KINETICS AND MECHANISM OF THE REACTION OF ALKYLATION OF BENZENE BY OLEFINS

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A great diversity of opinions exists concerning the mechanism of the alkylation of aromatic compounds by olefins. It is known that aluminum chloride catalyzes the addition of hydrogen halides to olefins [1]. The favorable effect of hydrogen halides on the alkylation of benzene by olefins has also been reported [2], which gives reason to suppose that the reaction proceeds through the intermediate formation of a halogenated derivative. However, another explanation appears very plausible, namely that the olefin itself can act as the alkylating agent owing to its power of forming, with aluminum chloride, complexes of the carbonium ion type by means of one of the double bond electron pairs [3]:

$$RCH{=}CH_2 + AlCl_3 \rightarrow R\overset{+}{C}H{-}CH_2 : \overset{-}{Al}Cl_3.$$

An extreme aspect of this viewpoint is the supposition that alkyl halides decompose during the reaction into hydrogen halide and olefins, only the latter being capable of alkylating the aromatic compound [4].

Not one of these opinions is supported by exhaustive proof, which we believed could be found by a study of the kinetics of the reaction.

EXPERIMENTAL TECHNIQUE

Measured volumes of purified benzene, nitrobenzene, and 10% aluminum chloride solutions in nitrobenzene were placed in a reaction flask and 60 ml capacity fitted with a sealed-in bubbler, gas exit tube, and a neck with a ground glass stopper. The required catalyst concentration and composition of the medium was obtained by variations of the amounts added (in all the subsequent experiments the benzene concentration was constant at 12.5%). The flask was placed in a thermostat in which a temperature of 30 ± 0.05° was maintained, and a stream of dry nitrogen was passed for 10 minutes through the reaction mass at a rate of about 60 ml per minute. Cyclohexene, prepared from cyclohexanol [5] (d_4^{20} 0.8110, n_D^{20} 1.4468), containing, according to analytical results [6], 99.13, 99.42% of cyclohexene, was added from a graduated pipet. The first sample was taken at once, after which the stream of nitrogen was stopped. Samples were taken for analysis at definite time intervals, and at those times the stream of nitrogen was reconnected for a short time in order to prevent the access of moisture from the air on removal of the stopper. The sample was transferred quickly with shaking to a flask with dilute hydrochloric acid, and a small excess of 0.1 N bromide-bromate solution was added. The flask was left to stand 15 minutes in the dark, 5 ml of 10% potassium iodide solution was added, and the iodine evolved was titrated by thiosulfate in presence of starch. This analytical technique was verified on previously prepared mixtures of benzene, cyclohexene, and nitrobenzene, and gave good results.

Cyclohexene and benzene in the presence of aluminum chloride give a good yield of phenylcyclohexane, which establishes the basis for the selection of this reaction for the kinetic investigation. However, cyclohexene can not only alkylate benzene by the action of aluminum chloride, but may polymerize [8]. This possibility was verified by keeping cyclohexene in a nitrobenzene solution of aluminum chloride at 30°. Titration of the samples showed that the content of cyclohexene in the solution is rather low in comparison with the value calculated from the amount taken, but remains constant for two hours.

Thus, the interfering effect of polymerization in the experimental conditions described is excluded. The low titration results are to be explained by the addition to the cyclohexene of hydrogen chloride formed by hydrolysis of the catalyst by the moisture remaining in the solvents or adsorbed by the aluminum chloride. This is confirmed by the following facts. When the concentration of the nitrobenzene solution of aluminum chloride was 0.1 mole/liter, the concentration of cyclohexene found was less than the calculated value for the given sample by 0.015 mole/liter, this difference being independent of the cyclohexene concentration. The addition of 0.04 mole/liter of hydrogen chloride (in nitrobenzene solution) to the mixture further decreased the cyclohexene concentration, also by 0.04 mole/liter. Already 0.5 minutes after the mixing, the addition proceeded to completion and no further change of the cyclohexene concentration occurred. This indicates the high rate of the addition reaction between hydrogen chloride and cyclohexene.

Effect of the cyclohexene and aluminum chloride concentrations

Results of experiments in which the effect of cyclohexene and aluminum chloride concentrations on the reaction rate was studied, are shown in Table 1.

Each value given is the mean from several experiments, the number of which is shown in Column 4, while the maximum deviation of the individual results from the mean is shown in Column 5.

TABLE 1

Line No.	Initial cyclohexene concentration, moles/liter	$AlCl_3$ concentration, moles/liter	Number of experiments	Deviation, moles/liter	Cyclohexene concentration in moles/liter for reaction times, minutes					Mean rate (moles/liter/minute)
					0.5	10	20	40	60	
1	0.305	0.203	4	±0.005	0.285	0.274	0.261	0.238	0.212	0.00122
2	0.203	0.203	4	±0.003	0.182	0.171	0.159	0.137	0.112	0.00116
3	0.101	0.203	3	±0.003	0.082	0.069	0.059	0.032	–	0.00123
4	0.203	0.100	4	±0.007	0.187	0.180	0.171	0.158	0.139	0.00079
5	0.203	0.049	3	±0.005	0.190	0.188	0.182	0.173	0.163	0.00043

Effect of hydrogen chloride concentration

The effect of hydrogen chloride on the reaction rate was studied by addition of different amounts of hydrogen chloride in nitrobenzene solution to the reaction mass. In these experiments the aluminum chloride concentration was 0.203 mole/liter and the initial cycohexene concentration, 0.203 mole/liter. The results obtained are shown in Table 2.

TABLE 2

Line No.	Concentration of hydrogen chloride added, moles/liter	Number of experiments	Deviation, moles/liter	Cyclohexene concentration in moles/liter for reaction times, minutes					Mean rate (moles/liter/minute
				0.5	10	20	30	40	
5	0.02	4	±0.005	0.160	0.135	0.109	0.082	0.052	0.00273
7	0.04	4	±0.004	0.141	0.100	0.057	0.012	–	0.00437
8	0.06	2	±0.004	0.121	0.067	0.014	–	–	0.00562

DISCUSSION OF RESULTS

The experimental results, shown in Fig. 1, indicate that the relationship between the cyclohexene concentration and the reaction time is in all instances expressed by straight lines. Lines 1, 2, and 3 show that their slopes are the same and that therefore the reaction rate does not depend on the cyclohexene concentration.

When hydrogen chloride is added to the reaction mixture, the rate of the process rises considerably, as can be seen by examination of Lines 6, 7 and 8 in comparison with 2 (Fig. 1). The total concentration of hydrogen halide should be equal to the sum of the hydrogen chloride added and that formed as the result of hydrolysis of aluminum chloride by moisture. This sum is equal to the intercept on the ordinate between the initial cyclohexene concentration and the point of intersection with the ordinate of the line for the variation of cyclohexene concentration with time. An examination of the reaction rate and the total hydrogen chloride concentration (Fig. 2) shows that the relationship between them is expressed by a straight line. Thus, the reaction rate is directly proportional to the hydrogen halide concentration:

$$v = k_1[HCl].$$

It should be pointed out that in all cases the effect of the hydrogen chloride concentration is taken to refer to its concentration before the addition of cyclohexene. During the reaction no hydrogen halide is present in the reaction mass, as it is instantaneously added on to cyclohexene to form cyclohexyl chloride.

A comparison of the Lines 2,4, and 5 (Figure 1) shows that the reaction rate increases with increase of aluminum chloride concentration, and the ordinate intercepts between the initial cyclohexene concentration (0.203 mole/liter) and the points of intersection of the lines with the ordinate axis are greater with higher aluminum chloride concentrations. This is to be explained by the fact that hydrogen chloride is formed not only by the action of the moisture in the solvents, but also by the action of moisture adsorbed by the solid catalyst used for perparation of the solutions. The hydrogen halide concentrations differed a little in these experiments, being 0.012, 0.015, and 0.020 mole/liter for aluminum chloride concentrations of 0.049, 0.100 and 0.203 mole/liter respectively. With this taken into account, we have the rate constants k_1 equal to 0.036, 0.052, and 0.60 respectively, so that when the aluminum chloride concentration is approximately doubled the reaction rate increases 1.2-1.5 times. This is in agreement with earlier data on the kinetics of the reaction of cyclohexyl chloride with benzene [3], the order of which with respect to the catalyst concentration has an average value of 0.5.

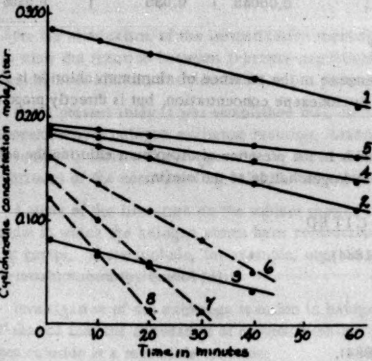

Fig. 1. Numbering as in Tables 1 and 2,

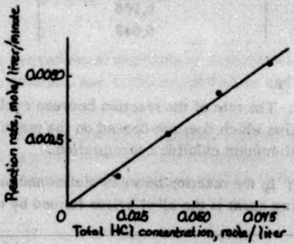

Fig. 2

It is possible to explain only in one way why the reaction rate is independent of the cyclohexene concentration and is directly proportional to the hydrogen chloride concentration. Obviously cyclohexene itself cannot react with benzene, since it does not enter the kinetic equation for the process. The influence of hydrogen chloride should be attributed to its power of adding on to cyclohexene to form cyclohexyl chloride. The latter is the true alkylating agent in the reaction.

$$C_6H_{10} + HCl \xrightarrow{AlCl_3} C_6H_{11}Cl, \qquad (1)$$

$$C_6H_{11}Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_{11}C_6H_5 + HCl. \qquad (2)$$

The first of these reactions, as was shown above, proceeds immeasurably rapidly. Therefore free hydrogen chloride is practically absent from the reaction mixture. Having been formed according to Reaction (2), it immediately reacts according to Equation (1). The rate of the process is determined by the last of the reactions given, in which the cyclohexene chloride concentration remains constant and equal to the concentration of hydrogen chloride added to the mixture or formed as the result of hydrolysis of the catalyst by moisture. Thus,

$$v = k_1[RCl] = k_1[HCl] = \text{const},$$

where k_1 is the rate constant for the first order reaction between cyclohexyl chloride and benzene.

Calculation of the rate constant for the first order reaction from the data obtained above, by division of the rate by the corresponding total hydrogen chloride concentration, gives the results shown in Table 3.

The last column of this table gives the rate constants k_1' for the reaction between cyclohexyl chloride and benzene, determined earlier [9] by direct measurements of the reaction kinetics in conditions equal to those used in the present study. The close agreement between this constant and the values calculated from data on the kinetics of the reaction between cyclohexene and benzene once again confirms the reaction mechanism assumed.

In our opinion, the reaction mechanism established in the present study is not limited to selected reaction conditions and choice of reagents, but may be generally extended to the alkylation of aromatic compounds by olefins in the presence of aluminum chloride.

TABLE 3

No.	$AlCl_3$ concentration (moles/liter)	Hydrogen chloride concentration moles/liter	Reaction rate (moles/liter/minute)	Rate constant k_1 min^{-1}	k_1' min^{-1}
1	0.203	0.020	0.0012	0.060	0.0642
2	0.203	0.040	0.00273	0.068	
3	0.203	0.060	0.00437	0.073	
4	0.203	0.080	0.00552	0.069	
5	0.100	0.015	0.00079	0.052	0.0470
6	0.049	0.012	0.00043	0.036	0.0308

SUMMARY

1. The rate of the reaction between cyclohexene and benzene in the presence of aluminum chloride is a constant value which does not depend on the reaction time or the cyclohexene concentration, but is directly proportional to the aluminum chloride concentration.

2. In the reaction between olefins and aromatic compounds in the presence of aluminum chloride the actual alkylating agent is the alkyl halide formed by the addition of hydrogen halide to the olefin.

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CATALYTIC TRANSFORMATIONS OF HALOGEN DERIVATIVES OF THE AROMATIC SERIES

II. EXCHANGE REACTIONS IN THE INTERACTION OF HALOGENATED NAPHTHALENES WITH HYDROGEN HALIDES

N. N. Vorozhtsov, Jr., and N. M. Przhiyalgovskaya

For the elucidation of the isomerization mechanism of halogen derivatives of naphthalene it appeared of interest to study the reaction between 1-bromo-napthalene and hydrogen chloride, and 1-chloronaphthalene and hydrogen bromide, over aluminum oxide in the vapor phase (at 350°).

In the present study it was established that, in these conditions, isomerization of halogenated naphthalenes is accompanied by a halogen exchange reaction: bromonaphthalene is partially converted into chloronaphthalene, and conversely*. Here and subsequently the terms chloronaphthalene and bromonaphthalene are applied to the isomeric mixtures of the corresponding halogenated napthalenes.

A study of the literature on the subject showed that similar exchange reactions have been described only for compounds in which the halogen atoms have considerable mobility and can in general be easily replaced by various atoms or groups. These include, for example, organic acid chlorides [1], di- and trinitrochlorobenzene [2, 3], and 2,3,5,6-tetrabromomethylquinol [4].

Investigation of the exchange reaction in halogenated derivatives in the aromatic series over aluminum oxide at 350° showed that the conversion of chloronapthalene by the action of halogen bromide into bromonaphthalene and hydrogen chloride is a reversible reaction:

$$C_{10}H_7Cl + HBr \xrightleftharpoons{Al_2O_3} C_{10}H_7Br + HCl.$$

Isomerization takes place simultaneously with the exchange reaction, and in consequence the reaction product contains both isomers, both of chloro- and bromonaphthalene.

The equilibrium proportions of the chloro and bromo derivatives are determined by the proportions of the starting substances. With the use of 5-6 moles of hydrogen bromide per 1 mole of 1-chloronaphthalene and 9-10 moles of hydrogen chloride per 1 mole of 1-bromonaphthalene, the halogen exchange in halogenated naphthalenes practically reaches 100% (see Figure).

The presence of a catalyst (aluminum oxide) is a necessary condition for the reaction. Without the catalyst, exchange (and isomerization) does not take place.

The exchange reaction, both in chloro- and in bromonaphthalene, is accompanied by the formation of naphthalene and its dihalogen derivatives. This may be explained by the fact that in both cases bromonaphthalene and hydrogen bromide are always present in the system. Naphthalene and its dihalogen derivatives are formed in consequence of the reversible nature of the reaction of naphthalene bromination [5]:

$$C_{10}H_7Br + HBr \rightleftharpoons C_{10}H_8 + Br_2.$$

The reversibility of the bromination reaction was first established by Faborsky in relation to bromine derivatives of the aliphatic series [6].

In order to determine the possibility of bringing about the exchange reaction in the benzene series, we carried out several experiments on the reaction of chlorobenzene with hydrogen bromide and of bromobenzene with hydrogen chloride. It was established that no halogen exchange takes place between chlorobenzene and hydrogen bromide at 400° over aluminum oxide. Under the same conditions bromobenzene is converted into chlorobenzene with 29.2% yield with a molar ratio of 1:7.3 between the bromobenzene and hydrogen chloride.

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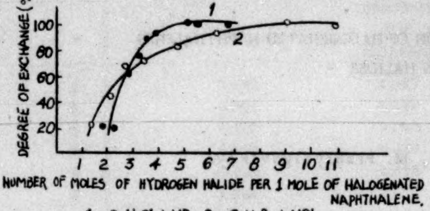
* The first experiments to establish the existence of this exchange reaction were performed by E. P. Fokin in 1951.



1 — $C_{10}H_7Cl$ + HBr, 2 — $C_{10}H_7Br$ + HCl.

Attempts to replace chlorine or bromine atoms in aromatic compounds by fluorine by passing a monohalogenated napthalene over aluminum oxide at 350° in the presence of hydrogen fluoride were not successful. It is interesting to note that fluorinated naphthalenes, on the contrary, exchange fluorine for chlorine fairly readily by the action of hydrogen chloride on them. For example, 1-fluoronaphthalene is converted into chloronaphthalene with 22.8% yield when fluoronapthalene is passed with 4.13 moles of hydrogen chloride, while 2-fluoronapthalene is converted into chloronaphthalene in 40.2% yield by the action of 3.75 moles of hydrogen chloride.

Thus, only hydrogen chloride and bromide take part in exchange reactions between halogenated naphthalenes and hydrogen halides over aluminum oxide. The exchange reaction does not take place with hydrogen fluoride.

In the course of the work it was established that the aluminum oxide used as catalyst reacts with HF at 350°, and is almost completely converted into AlF_3.

Analogous experiments with HCl showed that chemical action also takes place in this case. The activation of aluminum oxide by hydrogen chloride always results in the formation of a small amount of water and an increase of 1.7-1.9% in the weight of the catalyst.

Quite probably when the catalyst is treated with HCl (or HBr) the hydroxyl groups contained in it are replaced by halogen atoms with the formation of water. As the result of this reaction, Al-Cl groups appear on the catalyst surface, and these apparently act as the active centers.

EXPERIMENTAL

The experiments with hydrogen chloride or bromide were carried out in a quartz tube 1 meter long with 17 mm internal diameter. The tube was heated in an electric furnace 80 cm long, fitted with a contact thermometer and a relay, so that the desired temperature could be maintained to an accuracy of ± 3°. The catalyst used was technical active aluminum oxide which was activated before the start of the experiments by dry hydrogen halide for 1.5 hours at the experimental temperature of 350°. The volume occupied by the catalyst was as a rule 68-70 ml. Otherwise the experimental technique did not differ from that described previously [7].

The experiments with hydrogen fluoride were carried out in a steel tube. The amount of hydrogen fluoride passed was determined by the loss of weight of the HF cylinder. The rate of flow of the hydrogen fluoride was controlled by the number of bubbles in a polystyrene wash bottle sealed by vaseline oil.

The catalyzate was neutralized by dry soda and filtered, and then investigated. The course of the conversion was determined from the distillation results.

The 2-isomer content in the monochloro- and monobromonaphthalene fractions was determined from the solidification curves for binary mixtures of 1- and 2-isomers [5, 8].

When the exchange reaction took place, the degree of halogen substitution was determined by analysis of the acid gases leaving the reaction tube. The mixture of hydrogen fluoride with the chloride or bromide was analyzed argentometrically [9]. In the analysis of mixtures of hydrogen chloride and bromide, the difference between the densities of aqueous solutions of these gases at the same concentrations was used. Data for aqueous solutions of hydrogen bromide [10] and chloride [11] were used to plot $\underline{c} = \underline{f}(\underline{d})$ graphs, where $\underline{c}$ is the molar concentration and $\underline{d}$ the density of the solution. The molar composition of the mixture was determined graphically from the concentration of the solution and its density. The method was checked with synthetic mixtures of HCl and HBr. The relative error was ± 3% for 10-90% molar concentrations of HCl.

Conversion of 1-chloronaphthalene into bromonaphthalenes

0.85 mole (138 g) of 1-chloronaphthalene and 1-chloronaphthalene and 1.12 mole of hydrogen bromide was passed over aluminum chloride in 4 cycles of 3 hours each. Distillation of the catalyzate (137.5 g) yielded the following fractions: 1st, b.p. 215-220°, 21.7 g, solidif. p. 76.9°; 2nd, b.p. 220-256°, 4.7 g; 3rd, b.p. 256-263°, 41.6 g, solidif. p. 15.2°; 4th, b.p. 263-276°, 25.7 g; 5th, b.p. 277-283°, 9.2 g, solidif. p. 10.4°; residue 53 g.

The main fractions: 1st, 3rd, 5th, and the residue, were studied.

The 1st fraction in its constants corresponded to naphthalene. The amount of naphthalene (given here and subsequently as the sum of the weights of the 1st and 50% of the 2nd fractions) was 24.0 g (0.188 mole) or 22.1% molar on the 1-chloronaphthalene passed.

The 3rd fraction corresponded to the original monochloronaphthalene by its boiling point. When the fraction was cooled to 0°, a crystalline product was obtained from it, which after three recrystallizations from methanol formed shiny leaflets, m.p. 55-56°.

Found %: C 74.07, 74.13; H 4.48, 4.39. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.31.

The analytical data, and boiling and melting points of this substance agreed with those of 2-chloronaphthalene, while the fraction itself was a mixture of monochloronaphthalenes (with 47% of the 2-isomer).

The 5th fraction. When this was cooled to 0°, and filtered, a crystalline product was obtained, which melted at 54-55° after three recrystallizations from methanol. It formed white leaflets with a nacreous luster. The literature gives m.p. 56, 57, 58 and 59° [12] for 2-bromonaphthalene.

Found %: C 58.49, 58.43; H 3.44, 3.55. $C_{10}H_7Br$. Calculated %: C 58.00; H 3.41.

A mixed sample of this compound with 2-bromonaphthalene gave no melting point depression. However, the melting point was not depressed in a mixture with 2-chloronaphthalene either. According to literature data [12], 2-chloronaphthalene forms mixed crystals with 2-bromonaphthalene, and therefore, a mixture of the two shows no melting point depression [14]; therefore subsequently mixed sample melting points were not determined for the identification of these compounds.

A picrate with m.p. 78-79° was obtained from the compound. According to the literature, the melting point of 2-bromonaphthalene picrate is 79° [15].

The elementary composition of the mother liquor was also determined.

Found %: C 58.37, 58.25; H 3.49, 3.40. $C_{10}H_7Br$. Calculated %: C 58.00; H 3.41.

By its boiling point and elementary composition, the 5th fraction was a mixture of monobromonaphthalenes (with 48.5% of the 2-isomer).

The residue on cooling yielded a crystalline substance which melted at 155-156.5° after three recrystallizations from methanol. It formed white leaflets with a nacreous luster.

Found %: C 41.83, 41.92; H 2.25, 2.30. $C_{10}H_6Br_2$. Calculated %: C 42.00; H 2.12.

By its melting point and analytical data the compound corresponded to 2,6-dibromonaphthalene. The literature give m.p. 158° [16], 160° [17]. A mixed sample of this compound with known 2,6-dibromonaphthalene gave no melting point depression.

Reaction of 1-chloronaphthalene with hydrogen bromide in absence of catalyst. 18.4 g (0.113 mole) of 1-chloronaphthalene and 0.62 mole of hydrogen bromide was passed for 4 hours through a reaction tube filled with pieces of pumice previously treated with hydrochloric acid. The yield of catalyzate was 17.82 g (97%). The reaction product distilled completely in the range 254-259° (753 mm), n_D^{20} 1.6304, and was thus the original 1-chloronaphthalene.

Conversion of 1-bromonaphthalene into chloronaphthalenes

1-Bromonaphthalene was prepared by bromination of naphthalene [18]. The fraction used for the investigation had b.p. 275-280° (752 mm), solidif. p. +2°, n_D^{20} 1.6570, d_4^{20} 1.4915, content of the 2-isomer 3%.

0.196 mole (40.5 g) of 1-bromonaphthalene and 0.64 mole of hydrogen chloride was passed over aluminum oxide for 4 hours. Distillation of the catalyzate (31.2 g) yielded the following fractions: 1st, b.p. 215-220°, 4.8 g solidif. p. 76.3°; 2nd, b.p. 220-256°, 1.6 g; 3rd, b.p. 256-263°, 2.9 g solidif. p. 16.1°; 4th, b.p. 263-275°, 2.7 g; 5th, b.p. 275-282°, 2.5 g solidif. p. 10.2°; 6th, b.p. 285-305°, 4.0 g; residue 2.4 g.

The main fractions: 1st, 3rd, 5th and 6th, were investigated.

The 1st fraction was naphthalene. M.p. 77-79°. The amount of naphthalene was 5.6 g, or 22.4% molar of the 1-bromonaphthalene passed.

The 3rd fraction on cooling yielded a crystalline substance which melted at 55-56° after three recrystallizations from methanol.

Found %: C 73.93, 74.07; H 4.31, 4.49. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.31.

The boiling and melting point and the elementary composition of the substance showed it to be 2-chloronaphthalene. For identification, the picrate was prepared from the substance. This formed yellow needles, m.p. 80.3-81°. According to the literature the melting point of 2-chloronaphthalene picrate is 81.5° [15].

The liquid part of this fraction was separated into 3 fractions under vacuum. The middle fraction, b.p. 127° (12 mm) was analyzed.

Found %: C 73.26, 73.01; H 4.47, 4.62. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.31.

Therefore the 3rd fraction was a mixture of monochloronaphthalenes.

The 5th fraction on cooling yielded a crystalline product which melted at 56.2-57.1° after three recrystallizations from methanol. The picrate prepared from this compound melted at 78.2-78.9°. According to the literature, the melting point of 2-bromonaphthalene picrate is 79° [7]. The 5th fraction was a mixture of monobromonaphthalenes (with 48.5% of the 2-isomer).

The 6th fraction was separated by suction on a funnel into a crystalline substance and a liquid. The crystalline substance was recrystallized twice from methanol. It formed shiny leaflets, m.p. 137-139°.

Found %: C 49.51, 49.70; H 2.65, 2.52. $C_{10}H_6BrCl$. Calculated %: C 49.80; H 2.48.

By its composition, this substance was chlorobromonaphthalene. Several chlorobromonaphthalenes are described in the literature, but none corresponds to the melting point found. By analogy with the previous experiment we may assume that the compound is 2,6-chlorobromonaphthalene (not described in the literature). The liquid part of the fraction was not investigated.

Effect of the proportions of hydrogen bromide and 1-chloronaphthalene on the degree of halogen exchange. In this series of experiments the volume occupied by the catalyst was 100 ml. The molar ratio of 1-chloronaphthalene and hydrogen bromide was varied after every hour. The contact time varied in very wide limits (70-200 sec.), but all the experiments were carried out in a region far from the kinetic region, and therefore these variations could not affect the results. The experimental results are collected in Table 1 and shown in the Figure (Curve 1).

Effect of the proportions of hydrogen chloride and 1-bromonaphthalene on the degree of halogen exchange. The experiments were carried out in the same conditions as previously. The results are shown in Table 2 and in the Figure (Curve 2).

Reaction of chlorobenzene with hydrogen bromide. 14.1 g (0.125 mole) of chlorobenzene and 0.48 mole of hydrogen bromide was passed over aluminum oxide in 3 hours at 400°. The yield of catalyzate was .72 g (97.4%). The product distilled completely at 132-133° (755 mm), d_4^{20} 1.108, n_D^{20} 1.5263. The original chlorobenzene: d_4^{20} 1.108, n_D^{20} 1.5257.

Reaction of bromobenzene with hydrogen chloride. 45.9 g (0.292 mole) of bromobenzene and 2.14 moles of hydrogen chloride was passed in 2 cycles of 5 hours each over the catalyst at 400°. The yield of catalyzate was 40.2 g (87.7%). The product was distilled over a column 30 cm high and 12 mm internal diameter. The following fractions were obtained: 1st, b.p. 130-133°, 7.6 g, d_4^{20} 1.1073, n_D^{20} 1.5255; 2nd, b.p. 133-150°, 4.1 g, n_D^{20} 1.5471; 3rd, b.p. 150-155°, 20.8 g, d_4^{20} 1.4942, n_D^{20} 1.5597.

For identification of the 1st fraction, containing chlorobenzene, 1 g was nitrated by means of nitric acid [19] to the dinitro derivative. After recrystallization from dilute ethanol, yellow needle-like crystals with m.p. 50° were obtained. The literature gives m.p. 53° for dinitrochlorobenzene. No melting point depression was found in a mixed sample with known 2,4-dinitrochlorobenzene.

Reaction of 1-chloronaphthalene with hydrogen fluoride. 18 g (0.110 mole) of 1-chloronaphthalene and 18 g (0.9 mole) of hydrogen fluoride was passed over the catalyst in 3.5 hours at 350°. The yield of catalyzate was 14.59 g (81%).

TABLE 1

Experiment No.	Working period	Consumption of 1-chloronaphthalene (in moles)	HBr flow rate (ml/min)	Molar ratio of HBr to 1-chloronaphthalene	Amount of HCl formed (moles)	Degree of halogen exchange in 1-chloronaphthalene (in molar %)
1	I	0.0210	28	3.57	0.0185	88.2
	II	0.0251	21	2.24	0.0048	19.3
	III	0.0229	48	5.62	0.0228	100.0
2	I	0.0253	26	2.76	0.0158	62.4
	II	0.0310	21	1.82	0.0064	20.6
	III	0.0295	43	3.90	0.0275	93.0
3	I	0.0310	38	3.26	0.0232	74.8
	II	0.0274	54	5.27	0.0275	100.0
	III	0.0288	73	6.77	0.0263	98.0

TABLE 2

Experiment No.	Working period	Consumption of 1-bromonaphthalene (in moles)	HCl flow rate (ml/min)	Molar ratio of HCl to 1-bromonaphthalene	Amount of HBr formed (moles)	Degree of halogen exchange in 1-bromonaphthalene (in molar %)
1	I	0.0450	36	2.14	0.0191	42.4
	II	0.0536	54	2.70	0.0354	66.1
	III	0.0565	73	3.45	0.0401	71.0
	IV	0.0530	94	4.76	0.0434	81.9
2	I	0.0550	28	1.36	0.0118	21.4
	II	0.0276	65	6.30	0.0255	92.5
	III	0.0254	86	9.06	0.0253	100.0
	IV	0.0268	110	11.0	0.0259	97.0

The product distilled at 252-257° (749 mm) and solidified at − 1°. To show the presence of fluorinated derivatives in the reaction products, about 50 mg of the substance was fused with 3 times the amount of metallic potassium in a steel bomb [20]. A negative result was given by the qualitative reaction for fluorine with zirconium oxychloride in the presence of sodium alizarin sulfonate, which showed that no exchange reaction took place between chloronaphthalene and hydrogen fluoride.

The solidification point of the reaction product (−1°) corresponds to 33.3% content of 2-chloronaphthalene. When 1.56 g of 2-chloronaphthalene was added to 1.35 g of the product, the mixture solidified at 35.7°, which corresponds to 70% content of the 2-isomer. It was found by calculation that the original product contained 34% of 2-chloronaphthalene. The close agreement between the values found by the two determinations indicates once again that the reaction product was a mixture of monochloronaphthalenes only.

When the aluminum oxide was activated by hydrogen fluoride before the experiment, water was evolved. After the experiment the catalyst gained 60% in weight, lost its mechanical strength, and could not be regenerated. The composition of the catalyst indicated that it was almost completely converted into aluminum fluoride.

Found %: Al 36.3, 36.4; F 61.02, 58.20. AlF_3. Calculated %: Al 32.12; F 67.88.

Reaction of 1-bromonaphthalene with hydrogen fluoride. 34.8 g (0.167 mole) of 1-bromonaphthalene and 33 g (1.65 mole) of hydrogen fluoride was passed over the catalyst in 3 hours at 350°. The following fractions were collected during distillation of the catalyzate: 1st, b.p. 230-279°, 1.59 g, solidif. p. 33°; 2nd, b.p. 279-282°, 20.46 g, solidif. p. 7°. The gases leaving the reaction tube contained 0.0196 mole of hydrogen bromide. The 1st fraction was analyzed for fluorine content, by fusion of 70 mg of the substance with metallic potash in a steel bomb. A qualitative test of the melt by means of zirconium oxychloride gave a negative result, which indicated the absence of any exchange reaction between bromonaphthalene and hydrogen fluoride. The 2nd fraction contained 45.6% of the 2-isomer.

Reaction of 1-fluoronaphthalene with hydrogen chloride. 1-Fluoronaphthalene[*] prepared by the Balz and Schinemann method [22], had b.p. 216.3° (754 mm), solidif. p. −10.5°, n_D^{20} 1.5933.

Experiment 1. 28.3 g (0.18 mole) of 1-fluoronaphthalene and 20.2 g (0.56 mole) of hydrogen chloride was passed over aluminum oxide in 3 hours. Distillation of the catalyzate (20.9 g) yielded the following fractions (at 748 mm): 1st b.p. 213-214.5°, 14.7 g, n_D^{20} 1.5933 (1-fluoronaphthalene); 2nd, b.p. 218.5-251°, 1.8 g, n_D^{20} 1.6048 (intermediate fraction); 3rd, b.p. 253.4-254.5°, 2.4 g, n_D^{20} 1.6300 (monochloronaphthalene).

Experiment 2. The preceding experiment was repeated in order to determine the degree of conversion of 1-fluoronaphthalene into chloronaphthalene. 19.90 g (0.136 mole) of 1-fluoronaphthalene and 20.2 g (0.56 mole) of hydrogen chloride was passed over the catalyst. The catalyzate was distilled in the range 215-256° (756 mm). Yield 17.6 g.

63.10 mg sub.: 5.79 mg F; 3.62 mg Cl. Found %: $C_{10}H_7Cl$ 26.3; $C_{10}H_7F$ 75.0.

According to the analytical data, the reaction product contained 13.2 g (0.906 mole) of 1-fluoronaphthalene and 4.4 g (0.0270 g mole) of chloronaphthalene; hence the exchange of fluorine for chlorine proceeded to 22.8 molar %.

Reaction of 2-fluoronaphthalene with hydrogen chloride. 2-Fluoronaphthalene, prepared analogously to 2-fluoronaphthalene [23], had b.p. 217.8° (750 mm), solidif. p. 59.3°, m.p. 60.2-60.7°.

22.6 g (0.15 mole) of 2-fluoronaphthalene and 20.2 g (0.56 mole) of hydrogen chloride was passed over aluminum chloride in 3 hours. The following fractions were collected (at 750 mm) by distillation of the catalyzate (20.2 g) from an ordinary Wurtz flask: 1st, b.p. 216.5-219.5°, 2.7 g, solidif.p. 55.7° (2-fluoronaphthalene); 2nd, b.p. 220.5-250°, 10.8 g, solidif. p. 51.8° (intermediate fraction); 3rd, b.p. 252.5-256.5°, 3.5 g, solidif. p. 48.5° (monochloronaphthalene); residue 3.0 g.

The fluorine and chlorine contents of the 1st, 2nd, and 3rd fractions were determined (Table 3).

TABLE 3

Fraction	Weight taken (in mg)	Found		Found			
		F	Cl	$C_{10}H_7F$		$C_{10}H_7Cl$	
				(mg)	(%)	(mg)	(%)
1st	73.33	8.95	0.966	68.79	93.80	4.43	6.04
2nd	60.46	4.97	4.93	38.20	63.20	22.60	37.40
3rd	85.67	1.35	16.61	10.58	12.11	76.21	88.80

The following chloronaphthalene contents were calculated for the fractions from the analytical data: 1st, 0.166 g, 2nd, 4.04 g, 3rd, 3.11 g. Thus, the 3 fractions contained 9.73 g (0.0666 mole) of 2-fluoronaphthalene and 7.32 g (0.0449 mole) of chloronaphthalene, whence it follows that fluorine was exchanged for chlorine in 2-fluoronaphthalene by 40.2 molar %.

Reaction of aluminum oxide with hydrogen chloride. Active aluminum oxide in the form of a finely ground powder was placed in a test tube with a ground glass stopper and then put into a quartz tube heated in an electric furnace. The furnace temperature was measured by means of a theromocouple. The catalyst in the open test tube was dried in the tube in a stream of dry carbon dioxide at 350° to constant weight, and then subjected to the action of dry HCl. Hydrogen chloride was passed for 1 hour at the same temperature, and was then displaced from the tube by dry carbon dioxide to a negative reaction for hydrogen chloride. The test tube with the catalyst was weighed. The percentage increase in the dry weight of the catalyst was 1.71 and 1.92 (in two experiments).

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[*] The monofluoronaphthalenes were prepared by K. K. Babievsky; he also carried out the experiments on the reactions between monofluoronaphthalenes and hydrogen chloride.

An aqueous extract of the catalyst treated with HCl and then with CO_2 gave a copious white precipitate with silver nitrate solution.

SUMMARY

1. It was established that halogenated naphthalenes enter halogen exchange reactions with hydrogen chloride and bromide over aluminum oxide at 350°. 1-Chloronaphthalene was converted into bromonaphthalenes, and 1-bromonaphthalene and 1- and 2-fluoronaphthalenes into chloronaphthalenes.

2. Simultaneously with the halogen exchange, isomerization of the halogenated derivative takes place (as a result of which the reaction product contains both isomers of the monohalogenated derivative), and also conversion of part of the monohalogen derivative into naphthalene and polyhalogen derivatives.

3. Hydrogen fluoride does not enter into an exchange reaction with 1-chloro- and bromonaphthalene. Therefore the reaction between fluoronaphthalene and hydrogen chloride is irreversible, unlike the reaction between bromonaphthalene and hydrogen chloride.

4. The possibility of converting bromobenzene into chlorobenzene by the action of hydrogen chloride has been demonstrated.

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INVESTIGATION OF THE CATALYTIC CONVERSION OF ALCOHOLS INTO HYDROCARBONS OF THE DIVINYL SERIES

XVII. HEPTADIENE-1,3 AND HEPTADIENE-2,4 FROM A MIXTURE OF n-BUTYL ALCOHOL AND ACETONE

Yu. A. Gorin and F. A. Vasilyeva

A series of earlier papers described the formation of hydrocarbons with conjugate double bond systems from binary mixtures of various alcohols with carbonyl compounds by the action of Lebedev's catalyst, used in the preparation of divinyl from ethyl alcohol [1].

The addition of acetaldehyde to the ethyl alcohol increased the yield of divinyl calculated on the reacted alcohol [2], a mixture with acetone yielded piperylene [3], a mixture with methyl ethyl ketone gave hexadiene-2, 4 [4], a mixture of isobutyl alcohol with acetaldehyde gave 2-methylpentadiene-2,4 [5], a mixture of n-butyl alcohol with acetaldehyde gave hexadiene-2,4 [6], and a mixture of methyl alcohol with acetone, and also a mixture of isopropyl alcohol with formaldehyde, gave divinyl [7].

The formation of diethylenic hydrocarbons from mixtures of alcohols with carbonyl compounds with the use of aluminum oxide as catalyst was also observed by other workers. Ostromyslensky obtained divinyl from an equimolecular mixture of alcohol with acetaldehyde over this catalyst [8], and piperylene from mixtures of isopropyl or n-propyl alcohol with acetaldehyde [9].

Weizmann and Garrard [10] passed a mixture of n-butyl alcohol and acetone over aluminum oxide at 350°, and found heptadiene, methyl amyl ketone, and small amounts of butyraldehyde and isopropyl alcohol, in the reaction, products.

They attributed the formation of heptadiene to direct intermolecular dehydration of n-butyl alcohol and acetone, giving rise to methyl amyl ketone. Removal of water from the latter yielded heptadiene:

$$CH_3-CH_2-CH_2-CH_2\boxed{OH} + \boxed{H}CH_2-CO-CH_3 \xrightarrow{-H_2O}$$

$$\rightarrow CH_3-CH_2-CH_2-CH_2-CH_2-CO-CH_3 \xrightarrow{-H_2O} \text{heptadiene.}$$

These authors did not establish the structure of the heptadiene or a scheme for its formation.

We investigated the conversion of a mixture of n-butyl alcohol with acetone over Lebedev's catalyst, and found that the reaction products contained the diethylenic hydrocarbons C_7H_{12}, consisting of a mixture of heptadiene-1,3 and heptadiene-2,4 in a ratio of 2 : 1. The yield of C_7H_{12} hydrocarbons was 3.5% by weight, calculated on the sum of the reacted n-butyl alcohol and acetone.

In addition to the C_7H_{12} hydrocarbons, C_6 and C_8 hydrocarbons, and also butyraldehyde and isopropyl alcohol were found. Propylene and butylene were found in the gaseous products.

We explain the formation of heptadienes of the above structure on the basis of the principles of a scheme for the formation of divinyl from ethyl alcohol, which was put forward and experimentally established in a series of earlier papers by one of the present authors [11, 12, 13].

We assume that the conversion of other alcohols by the action of Lebedev's catalyst, and also of binary mixtures of various alcohols and of binary mixtures of alcohols with carbonyl compounds, into hydrocarbons with conjugated double bond systems, follow the same mechanism [13]. These reactions are based on condensation of carbonyl compounds, which are either formed by dehydration of the original alcohols, or are introduced in mixtures with the various alcohols. The condensation is accompanied by the removal of water and the formation of unsaturated aldehydes or unsaturated ketones, according to the nature of the alcohols or carbonyl compounds used. Subsequent conversions of the condensation products by reduction to unsaturated alcohols followed by dehydration lead to the formation of hydrocarbons with conjugated double bond systems.

The formation of heptadienes from a mixture of n-butyl alcohol with acetone may be represented by the following scheme.

1. Conversion of n-butyl alcohol into butyraldehyde by the action of the dehydrogenating component of the catalyst

$$CH_3CH_2CH_2CH_2OH \rightarrow H_2 + CH_3CH_2CH_2CHO.$$

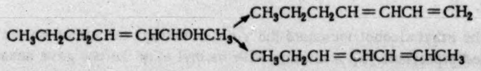
2. Condensation of butyraldehyde with acetone to give butylideneacetone*

$$CH_3CH_2CH_2CHO + CH_3COCH_3 \rightarrow [CH_3CH_2CH_2CHOHCH_2COCH_3] \rightarrow$$
$$\rightarrow H_2O + CH_3CH_2CH_2CH{=}CHCOCH_3.$$

3. Reduction of butylideneactone by butyl alcohol to an unsaturated secondary alcohol

$$CH_3CH_2CH_2CH{=}CHCOCH_3 + 2H \rightarrow CH_3CH_2CH_2CH{=}CHCHOHCH_3.$$

4. Dehydration of the secondary alcohol, accompanied by a regrouping of the double bonds and the formation of two isomers – heptadiene-1,3 and heptadiene-2,4



$$CH_3CH_2CH_2CH{=}CHCHOHCH_3 \begin{array}{l} \nearrow CH_3CH_2CH_2CH{=}CHCH{=}CH_2 \\ \searrow CH_3CH_2CH{=}CHCH{=}CHCH_3 \end{array}$$

It is possible that (I) is the primary dehydration product, which isomerizes to the more stable (II) with a conjugate system in the middle of the carbon chain. Examples of similar reactions have been described by Prevost [14] and Dumoulin [15].

5. The formation of isopropyl alcohol is explained by the reduction of acetone by butyl alcohol

$$CH_3COCH_3 + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CHOHCH_3 + CH_3CH_2CH_2CHO.$$

The dehydration of the original butyl alcohol, and also of the isopropyl alcohol formed, results in the formation of butylene and propylene, found in the gaseous reaction products.

The C_6 hydrocarbons are formed by the condensation of two molecules of acetone [16], and the C_8 hydrocarbons by the condensation of two molecules of butyraldehyde [17]. These hydrocarbons were not investigated in detail in the present work.

Small amounts of heptadiene were found among the by-products of divinyl production from ethyl alcohol by Lebedev's method [18]. The results of the present study explain its formation in this process. It is known that, in addition to divinyl, butyraldehyde, acetone, and butyl alcohol are formed as by-products. Interaction of these substances and their subsequent conversion by the action of Lebedev's catalyst should lead to the formation of heptadienes with the structure shown above.

It should be pointed out that the formation of a diene hydrocarbon by dehydration of methyl amyl ketone over Al_2O_3 according to Weizmann and Garrard's scheme [10] seems improbable. If such a reaction took place, the evidently divinyl could be obtained from methyl ethyl ketone by dehydration over Al_2O_3. However, such a reaction is not known.

It follows from Weizmann and Garrard's data that in their experiments acetone was reduced by butyl alcohol with the formation of isopropyl alcohol and butyraldehyde. The reduction of carbonyl compounds by alcohols through hydrogen redistribution, which occurs in the conditons of Lebedev's process [11, 13, 18], also apparently takes place under the influence of aluminum oxide which was used by Weizmann and Garrard; therefore the butylideneacetone formed by the action of Al_2O_3 from acetone and butyraldehyde should be reduced to an unsaturated secondary alcohol, which could subsequently be completely dehydrated to heptadiene.

The formation of methyl amyl ketone observed by Weizmann and Garrard is the result of intramolecular regrouping which may occur in the unsaturated secondary alcohol formed in the intermediate stage by the reduction of butylideneacetone by butyl alcohol

$$CH_3CH_2CH_2CH{=}CHCOCH_3 + 2H \rightarrow CH_3CH_2CH_2CH{=}CHCHOHCH_3 \rightarrow CH_3CH_2CH_2CH_2CH_2COCH_3.$$

Similar isomerization by the action of aluminum oxide was studied by Weston and Adkins [19] in the case of allyl alcohol, which was thereby converted into propionic aldehyde.

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* It must be pointed out that Weizmann and Garrard found butylideneacetone in the reaction products when a mixture of butyraldehyde with acetone was passed over aluminum oxide at 350°.

Thus, by means of our proposed scheme it is possible to explain all the reactions observed by Weizmann and Gerrard with the closest approach to reality.

EXPERIMENTAL

n-Butyl alcohol (b.p. 116.8-117.8°, d_4^{20} 0.8019, n_D^{20} 1.3985) and acetone (b.p. 56-57°, d_4^{20} 0.7915, n_D^{20} 1.3582), were used.

In order to determine the conditions favoring the formation of C_7 diethylenic hydrocarbons, preliminary experiments were carried out with mixtures of butyl alcohol and acetone (1: 1 and 1: 2 molar) over mixed Lebedev's catalysts, containing the dehydrogenating and dehydrating components in different proportions. The experiments were carried out with the aid of the tubular furnace described earlier [20]. 200 ml of the catalyst was placed in the furnace. The highest yields of hydrocarbons with conjugate double bond systems (as shown by the formation of a white precipitate of polymer sulfone by the action of SO_2) were found with the use of a catalyst of modified composition (increased dehydrogenating and decreased dehydrating component contents) at 380° and with a 1: 1 molar ratio of n-butyl alcohol to acetone.

A series of experiments was carried out in order to accumulate the reaction products under the conditions chosen. In each of these experiments a mixture of n-butyl alcohol and acetone was passed through the furnace in 200 ml portions at a rate of 1 ml per minute. After the experiment the catalyst was regenerated by air for 1 hour at 525°. A portion of gas was collected in each experiment to make up an average sample. The liquid products were combined; the hydrocarbons were separated from the aqueous layer and washed with water, to remove unreacted butyl alcohol and other soluble products, to constant volume. The aqueous layer and the wash waters were combined and n-butyl alcohol, acetone, and other reaction products were obtained from them by distillation.

A total amount of 1920 g of mixture (1068 g of n-butyl alcohol and 852 g of acetone) was passed. 343.5 g of butyl alcohol and 305 g of acetone was returned unchanged. 531.2 g of water-insoluble products was obtained. The total yield of washed hydrocarbons was 27.8% by weight calculated on the mixture passed, and 41.8% by weight on the sum of the reacted n-butyl alcohol and acetone (1271.5 g).

Investigation of the Reaction Products

a) The average gas sample had the following composition (in vol %): CO_2−7.7; CO−0.61; H_2−22.8; C_3H_6−25.5; C_4H_8−38.2 (propylene and butylene were determined by distillation over a Podbelniak type column).

b) The fraction up to 99° was distilled from the combined aqueous solution. The upper layer of the distillate was separated off, and the lower aqueous layer was salted out by potash; the upper layer which separated out was combined with the previous one. The product was dried by potash and distilled over a column. The following fractions were collected: 1st, b.p. 56-58° (acetone), d_4^{20} 0.793; 2nd, b.p. 73-80° (butyraldehyde), d_4^{20} 0.818; 3rd, b.p. 82-84.5° (isopropyl alcohol), d_4^{20} 0.791; 4th, b.p. 115-116° (butyl alcohol), d_4^{20} 0.811.

Acetone was determined by Chelintsev's method [21] with the aid of furfural after preliminary oxidation of the aldehydes by moist silver oxide [22]. The presence of butyraldehyde was proved by the preparation of 2,4-dinitrophenylhydrazone with m.p. 120.5° (122° according to the literature). Isopropyl alcohol was identified by the preparation of isopropyl acetate: the boiling point and the density of the ester obtained agreed with the literature data.

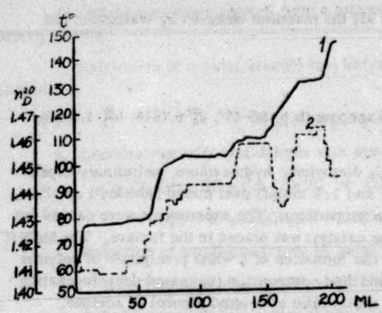
The upper condensate layer, in 531.2 g yield after being washed to constant volume, was dried with calcium chloride, boiled 8 hours over sodium, and distilled in a nitrogen atmosphere from a flask with a double bulb dephlegmator. 457.3 g was used for the distillation.

The following fractions were obtained: 1st, b.p. 56-90°, 6.6%; 2nd, b.p. 90-110°, 23.4%; 3rd, b.p. 110-126°, 22.2%; residue and losses, 47.8%.

The 2nd and 3rd fractions were combined and distilled over a metal cap column (50 theoretical plates).

The distillation results are shown in the figure, which, in addition to the distillation curve, shows refractometric data (the abscissa axis shows the amount of the fractions in milliliters, and the ordinate axis, the boiling points and n_D^{20}).

As the figure shows, the distillation yielded 4 fractions, corresponding to hydrocarbons of different compositions: 77-78°-C_6; 103-103.6° and 109.2-109.7°-C_7; 132-133°-C_8.



Hydrocarbon distillation curves.
1) Distillation curve, 2) refraction curve.

Investigation of the 103-103.6° fraction

By its boiling point this fraction was close to heptadiene-1,3.

n_D^{20} 1.4422, d_4^{20} 0.7297, MR_D 34.86. C_7H_{12}. Calc. 33.57; EMR_D 1.29.

0.2276 g sub.: 0.7335 g CO_2; 0.2571 g H_2O. 0.1534 g sub.; 26.16 g benzene Δt 0.34°. Found %: C 87.88; H 12.64. M 94.5. C_7H_{12}. Calculated %: C 87.41; H 12.59. M 96.

Literature data for heptadiene-1,3: b.p. 100.55° (747.6 mm), d_4^{20} 0.7222, n_D^{20} 1.4428 [23].

Hydrogenation of the 103-103.6° fraction. 0.5937 g of the hydrocarbon in alcohol solution with 0.1 g of platinum black was hydrogenated by 251 ml of hydrogen (NTP). Found: diethylenic hydrocarbons 81.2%, ethylenic 18.8%.

The saturated hydrocarbon formed by the hydrogenation of 3.9 g of the 103-103.6° fraction, was washed free from alcohol by saturated common salt solution, dried by calcium chloride, and distilled over sodium. The main mass distilled at 98.2°.

d_4^{20} 0.6877, n_D^{20} 1.3887.

0.1836 g sub.: 0.5679 g CO_2; 0.2644 g H_2O. 0.1145 g sub.; 19.26 g benzene: Δt 0.325°. Found %: C 84.35; H 16.13, M 99.1. C_7H_{16}. Calculated %: C 83.89; H 16.11, M 100.2.

Literature data for n-heptane: b.p. 98.4°, d_4^{20} 0.6837, n_D^{20} 1.3877 [24].

The hydrogenation product of the 103-103.6° fraction was normal heptane, and therefore the original unsaturated hydrocarbon had a normal carbon chain.

Action of sulfur dioxide solution on the 103-103.6° fraction. By the action of aqueous sulfur dioxide solution on a sample of the fraction, a white cake of amorphous polymer sulfone was formed (characteristic for hydrocarbons with conjugate double bond systems).

Ozonation of the 103-103.6° fraction. 2 g of the freshly distilled hydrocarbon in chloroform solution was ozonized by Yakubchik's method [25], developed for the determination of vinyl groups in rubbers. After removal of chloroform from the ozonides under vacuum, water was added to the residue heated to 25°, and the mixture was heated 3 hours on the water bath to decompose the ozonides. Formaldehyde was determined quantitatively in the ozonolysis products by means of the reaction product with β-naphthol [26], and formic acid was determined from the calomel precipitate formed by heating the sample with mercuric chloride solution [27]. By these determinations it was possible to determine the content of the $CH_2=C<$ end group in the hydrocarbons studied and to indicate the amount of diethylenic hydrocarbon with a conjugate system in the 1,3 position.

Found: formaldehyde 0.2%, formic acid 80.4%, calculated on C_7H_{12}.

The results show that the substance investigated contained 80.6% of a hydrocarbon with a double bond at the end of the chain, and therefore, with a conjugate system in the 1,3 position. The diethylenic hydrocarbon content determined by hydrogenation (81.2%) was close to the results found by ozonolysis. The remainder was probably the C_7 ethylenic hydrocarbon with the double bond in the middle of the chain, the formation of which may be assumed in this process (for example, in the Lebedev reaction some pseudobutylene is formed from ethyl alcohol, in addition to divinyl [1]).

Condensation of the 103-103.6° fraction with maleic anhydride. 0.8 g of maleic anhydride in benzene solution was added to 0.85 g of the fraction freshly distilled over sodium. The mixture was left to stand for 24 hours and the benzene was distilled off by warming in vacuum. The reaction product was washed with cold water. Water was removed from the remaining oil by heating to 90° in vacuum. Pale yellow crystals separated on cooling. After 3-fold recrystallization from benzene they melted at 50°.

0.0714 g sub.; 25.38 g benzene: Δt 0.08°. Found: M 192.9. $C_{11}H_{14}O_3$. Calculated: M 194.

Investigation of the 109.2-109.7° fraction

By its boiling point this fraction corresponded to heptadiene-2,4:

d_4^{20} 0.7386, n_D^{20} 1.4582, MR_D 35.44, C_7H_{12}. Calc. 33.57; EMR_D 1.87.

0.2130 g sub.: 0.6835 g CO_2; 0.2372 g H_2O. 0.1911 g sub.: 27.30 g benzene: Δt 0.303°. Found%: C 87.51; H 12.46. M 94.6. C_7H_{12}. Calculated %: C 87.41; H 12.59. M 96.

Literature data for heptadiene-2,4 [28]: b.p. 109.6°, d_4^{20} 0.7384, n_D^{20} 1.4578.

An amorphour white cake of polymer sulfone was formed by the action of aqueous sulfur dioxide solution on the 109.2-109.7° fraction.

The condensation product of the 109.2-109.7° fraction with maleic anhydride in benzene solution (after removal of benzene, washing with water to remove unreacted maleic anhydride, and 4-fold recrystallization) melted at 69.5°; according to the literature the melting point of the maleic anhydride adduct with heptadiene-2,4 is 70.5° [28].

Investigation of the Raman spectra of the 103-103.6° and 109.2-109.7° fractions

The combinational light scattering (Raman) spectra were studied by means of visual estimation of intensity.

Spectral analysis data for the 103-103.6° fraction (in cm^{-1}): 1106 (3), 1163 (4), 1181 (3), 1300 (3), 1374 (3), 1449 (2), 1609 (3), 1655 (10).

The 1609 and 1655 frequencies and their high intensities indicate the presence of a conjugate double bond system. Owing to lack of literature data on the spectrum of heptadiene-1,3 we compared our results with the spectral frequencies for pentadiene-1,3. Slobodin and Shokhor [29], and Slobodin and Khokhlacheva [30] found the frequencies 1569, 1603, 1646, 1655, for pentadiene-1,3, which probably correspond to the cis form (1596 and 1646) and the trans form (1603 and 1655). Apparently the fraction investigated by us contains heptadiene with a conjugate system in the 1,3 position, corresponding to the trans form (1609 and 1655).

Spectral analysis data for the 109.2-109.7° fraction (in cm^{-1}): 850 (3), 889 (2), 962 (1), 1010 (2), 1058 (2), 1086 (3) 1115 (6), 1149 (8), 1172 (10), 1201 (5), 1253 (8), 1276 (4), 1300 (6), 1308 (5), 1449 (6), 1512 (1), 1563 (3), 1600 (4), 1659 (20), 1664 (20).

The frequencies 1659 and 1664 and their high intensities indicate the presence of a conjugate double bond system. A comparison of these frequencies with the frequencies 1654 and 1663 in the spectrum of heptadiene-2,4, determined by Treshcheva, Tatevsky, Levina, and others [31], and also with the frequencies 1656 and 1668 in the spectrum of hexadiene-2,4, obtained by Tatevsky, Treshcheva, Skvarchenko, and Levina [32] leads to the conclusion that the heptadiene studied has a conjugate double bond system in the 2,4 position.

Investigation of the other hydrocarbon fractions

The fractions corresponding to the C_6 hydrocarbons were collected by means of the distillation column in the ranges 77-77.5° and 77.5-78°. Their d, n, and MR were determined, and also the diethylenic hydrocarbon content by hydrogenation over platinum. It was shown that these fractions contained a mixture of ethylenic and diethylenic C_6 hydrocarbons, formed by conversion of acetone in the given conditions [16].

The 132-133° fraction by the results of d, n, and MR determinations and from the hydrogenation results, corresponds to a mixture of C_8H_{14} and C_8H_{16} hydrocarbons, the conversion products of n-butyl alcohol over Lebedev's catalyst. These hydrocarbons were studied by us previously [17], and therefore they were not investigated in greater detail.

We express our gratitude to Ya. M. Slobodin for assistance in investigation of the Raman spectra.

SUMMARY

1. The conversion of a mixture of n-butyl alcohol with acetone into C_7H_{12} hydrocarbons with conjugate double bond systems over mixed Lebedev's catalyst has been studied.

2. It was established that the hydrocarbons formed have a normal carbon chain, and are heptadiene-1,3 and heptadiene-2,4. These hydrocarbons are formed in a 2 : 1 ratio.

3. The reaction products also contain butyraldehyde, isopropyl alcohol, butylene, propylene, and also C_6 hydrocarbons (by acetone conversion) and C_8 hydrocarbons (by butyl alcohol conversion).

4. A scheme is put forward for the catalytic conversion of a mixture of n-butyl alcohol with acetone into diethylenic C_7H_{12} hydrocarbons, based on the concept of mixed condensation of butyraldehyde with acetone to give butylideneacetone, followed by its reduction by butyl alcohol to an unsaturated alcohol, and dehydration of the latter to form the isomeric heptadienes (1, 3 and 2, 4).

5. An explanation is given for the formation of heptadiene as a by-product in the catalytic conversion of ethyl alcohol into divinyl by Lebedev's method.

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THE HYDROGENATION RATE OF AROMATIC HYDROCARBONS

VIII. HYDROGENATION OF CONDENSED AROMATIC HYDROCARBONS IN THE PRESENCE OF TUNGSTEN DISULFIDE

A. V. Lozovoi and S. A. Senyavin

In the previous communication[1] we described the results of measuring the relative hydrogenation rates of benzene and a number of its homologs under high hydrogen pressure, at elevated temperature, and in the presence of WS_2 as catalyst. Then we studied the hydrogenation rates of the condensed aromatic hydrocarbons and their hydro derivatives. These compounds are found in the products obtained from the liquid phase hydrogenation of coal and primary tars, and are also contained in appreciable amounts in petroleum and the products of its refining. As is known, in the second, the so-called vapor phase step in the destructive hydrogenation of fuel oil, carried out in the presence of WS_2 as catalyst, the material subjected to hydrogenation is the oil fraction, containing the indicated hydrocarbons, obtained in the first, liquid phase stage of the process.

While some data for the relative hydrogenation rates of the simpler condensed aromatic hydrocarbons — naphthalene, anthracene, phenanthrene, acenaphthene — in the presence of $Ni + Al_2O_3$ and MoS_2 catalysts exist in the literature [2,3,4], analogous information for their hydrogenation over WS_2 is available in neither the Soviet nor the foreign literature. In the meantime, a study of the hydrogenation kinetics of condensed aromatic hydrocarbons in the presence of WS_2 is of essential interest, since it is the basic catalyst in the vapor phase steps of the commercial process for the destructive hydrogenation of fuel oil.

In the present communication are given the results of determining the relative hydrogenation rates at 400°, a pressure of 150 atm, in the presence of WS_2, of naphthalene into tetralin, anthracene into di-, tetra- and octahydroanthracenes, and also of chrysene into some of its hydro derivatives, in comparison to the hydrogenation rate of benzene.

Method of Study and its Objectives

The method of measuring the hydrogenation rates of condensed aromatic hydrocarbons in principle was the same as that described in previous communications [1,7]. Calculation of the amount of hydrogenated hydrocarbon was essentially based on the method of measuring the amount of reacted hydrogen. To the rotated hydrogenation autoclave, having a volume of 0.6 liters, was connected a 0.125 liter calibrated high pressure hydrogen bomb. As the hydrogen was used up in the autoclave and the pressure fell the needed amount of hydrogen was added from the bomb, measured by the reading of the control manometer (with a scale division of 2 atm) on the bomb. The used method assured measurement of the degree of hydrogenation to an accuracy of not less than ± 1%, and in most of the experiments the accuracy was greater than this.

The characteristics of the hydrocarbons used in the experiments are given in Table 1.

A fresh portion of the WS_2 catalyst, described in the previous communication [1], was used in each experiment, in an amount ranging from 1.5 to 40% on the weight of hydrocarbon being hydrogenated. Electrolytic hydrogen was used in the hydrogenations.

The degree of hydrocarbon hydrogenation toward the end of the experiment failed to exceed 80%. The experiment was prolonged for 60 to 90 minutes, in which connection the reaction rate was measured every 5 to 30 minutes.

At the beginning of hydrocarbon hydrogenation the reaction rate dropped somewhat, but it quickly stabilized and during the period of making measurement it remained constant or dropped slowly in the majority of cases. The decrease in the hydrogenation rate at the beginning of the experiment was apparently due to the reduction of the WS_3, present in the catalyst and possessing a higher activity than the less active but more stable WS_2.

The reaction rate was expressed in moles of hydrocarbon reacted in one minute. Inasmuch as the reaction rate during the time of measurement was practically constant, the molar amount of hydrocarbon, hydrogenated per unit of

TABLE 1

Exp. No.	Hydrocarbons	Melting point	Boiling point	n_D^{20}	Method of Preparation
1	Benzene	–	79.75–80.0° (761 mm)	1.5000	–
2	Tetralin	–	205–207 (758 mm)	1.5411	–
3	Naphthalene	80.5°	–	–	Purified with 5% Na at 120-130°
4	Anthracene	214–215	–	–	–
5	9,10-Dihydroanthracene	103–110	–	–	Anthracene hydrogenated to the addition of 1 mole of H_2 per mole of compound in the presence of WS_2 at 400° and 150 atm.
6	Tetrahydroanthracene, white crystals	–	–	–	9,10-Dihydroanthracene hydrogenated under the above indicated conditions with the addition of 1 mole of H_2 per mole of compound
7	Octahydroanthracene, white crystals, probably a mixture of symmetrical and unsymmetrical octahydroanthracene*	Crystallizes on standing	290–295	1.5588	Tetrahydroanthracene hydrogenated under the same conditions to the addition of $2H_2$ per mole of compound. Elementary composition: C-90.18%, H-9.82%; calculated for $C_{14}H_{18}$: C-90.22%, H-9.78%.
8	Chrysene, yellow crystals	249–252°	–	–	–
9	Tetrahydrochrysene (structure not established), light yellow crystals	128–136	–	–	Chrysene hydrogenated under the above indicated conditions to the addition of $2H_2$ per mole of compound
10	Octahydrochrysene, a mixture of isomers	–	290–380: 300–154%, 300–320, 192% 320–340, 192% 340–370, 27%	1.5660	Tetrahydrochrysene hydrogenated under the above indicated conditions to the addition of $2H_2$ per mole of compound

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* The simultaneous formation of the symmetrical and unsymmetrical octahydroanthracene in the hydrogenation of tetrahydroanthracene in the presence of MoS_2 was shown by Prokopets and coworkers [4]. The hydrogenation in the presence of WS_2 probably proceeds in a similar manner. According to the literature [5], the boiling point of the symmetrical octahydroanthracene is 293 - 295°, of the unsymmetrical it is 292-295°.

time, served as a direct expression of the reaction rate constant for the hydrogenation of the investigated hydrocarbon. The ratio of the latter to the rate constant for the hydrogenation of benzene, taken as 100 (or tetralin as 250) [1], expressed the relative hydrogenation rate of condensed aromatic hydrocarbons and their partially hydrogenated products.

In the gases, remaining in the autoclave after measuring the hydrogenation rates for the hydrogenated derivatives of anthracene and chrysene, we failed to detect the presence of any methane hydrocarbons, with the exception of the hydrogenation of octahydrochrysene, where in the gas after hydrogenation there was found 2% of C_nH_{2n+2} hydrocarbons. This indicates incipient destruction of the hydrogenated chrysene derivatives, as a result of which the hydrogenation of chrysene was terminated at the dodecahydrochrysene stage, after 65% of the theoretical amount of hydrogen had been absorbed.

DISCUSSION OF RESULTS

In Table 2 are given the experimental data on the hydrogenation rate of naphthalene into tetralin into decalin, and of anthracene and three of its hydro derivatives in comparison to the naphthalene hydrogenation rate; in Table 3, the rates for the hydrogenation of chrysene and its hydro derivatives are compared with the hydrogenation rate for benzene. In Table 4 are given the summarized measurement results for the relative hydrogenation rates of nine studied hydrocarbons, in which connection in some of the cases the hydrogenation rate is compared with the corresponding values obtained for hydrogenation in the presence of MoS_2 [7] and Ni + Al_2O_3 [2].

As can be seen from the data in Table 4, the hydrogenation kinetics for condensed aromatic hydrocarbons is characterized by complexity and specificity. For the simpler members of these hydrocarbons — naphthalene, anthracene, and also acenaphthene and phenanthrene (their hydrogenation rate was studied in the presence of Ni + Al_2O_3 [2]) it is characteristic for the reaction to proceed in stepwise fashion through successive hydrogenation stages — into the di-, tetra-, octa- and perhydro derivatives. The first hydrogenation stages in the presence of all of the hydrogenation catalysts studied by us proceed with considerable rapidity, being ten times as great as the hydrogenation rate in the last stages, when the benzene ring is saturated.

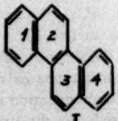
On passing to a more complex aromatic hydrocarbon, namely chrysene, the kinetics of high temperature hydrogenation in the presence of WS_2 changes: the hydrogenation loses its stepwise nature with an extremely high initial and gradually decreasing (in measure with the degree of hydrogenation) rate, and from the very beginning the reaction proceeds slowly at a constant rate, somewhat slower than the hydrogenation rate of benzene and 30-60 times slower than the hydrogenation rates of naphthalene and anthracene. The practically constant hydrogenation rate of chrysene was retained up to 65% of the theoretical amount of hydrogen absorption. The structure of chrysene (I) predicates the possibility of either the successive or the simultaneous hydrogenation of synonymous rings 1 and 4. Judging from the constancy of the rate for the addition of the first eight hydrogen atoms, it is more probable to assume the simultaneous hydrogenation of these two rings with the direct formation of octahydrochrysene. The transition to the hydrogenation of the octahydrochrysene is accompanied by a certain change in the reaction rate. But since the structure of the equivalent rings 2 and 3 in octahydrochrysene fails to differ in principle from the structure of rings 1 and 4 in the chrysene molecule, then a considerable change in the reaction rate is not observed, such as is revealed in the transition from the initial to the last stages in the hydrogenation of naphthalene and anthracene. Also, there is no basis to expect a reduction in the reaction rate on further hydrogenation, in the presence of

TABLE 2

Relative Hydrogenation Rates of Naphthalene, Anthracene and Their Hydro Derivatives

Temperature 400°, Pressure 150 Atm., Catalyst WS_2

Exp. No.	Hydrocarbon and Studied Reaction	Amount of Catalyst (in Wt. %)	Duration of Experiment (in Min.)	Amount of Hydrogenated Hydrocarbon (in Moles)	$K_0 \cdot 10^4$ $\frac{mole}{min} \cdot 10^4$	Relative Hydrogenation Rate (Hydrogenation Rate of Benzene 100)
1	Naphthalene, 40 g, hydrogenation to tetralin	10.0	60	0.249	41.5	2300*
2	Tetralin, 40 g, hydrogenation to decalin	10.0	60	0.027	4.5	250**
3	Naphthalene, 40.g, hydrogenation to tetralin	1.5	84	0.133	15.8	2300
4	Anthracene, 40 g, hydrogenation to dihydroanthracene	1.5	44	0.187	42.5	6187
5	Naphthalene, 34 g, hydrogenation to tetralin	1.5	84	0.113	13.5	2300
6 7	9, 10-Dihydroanthracene, 32.8 g and 34.9 g, hydrogenation to tetrahydroanthracene	1.5	90	0.068	7.6	1295
8	Naphthalene, 31.2 g, hydrogenation to tetralin	10.0	60	0.194	32.3	2300
9	Tetrahydroanthracene, 31.2 g, hydrogenation to octahydroanthracene	10.0	60	0.0379	6.3	449
10 11 12	Naphthalene, 17 g, hydrogenation to tetralin	10.0	60	0.0993	16.6	2300
13	Octahydroanthracene, 17 g, hydrogenation to perhydroanthracene	10.0	60	0.01264	2.1	291



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* Calculated from the hydrogenation rate of tetralin.

** [1].

TABLE 3

Relative Hydrogenation Rates of Chrysene and Its Hydro Derivatives in the Presence of WS_2 (40%)

Temperature 400°, Pressure 150 Atm., Duration of Experiments 60 Minutes

Exp. No.	Hydrocarbon and Studied Reaction	Amount of Hydrocarbon Hydrogenated in the Exp. Time (in Moles)	$K_0 \cdot 10^4 \left(\frac{\text{mole}}{\text{min}} \cdot 10^4\right)$	Relative Hydrogenation Rate
14	Benzene, 30 g	0.0576	9.6	Taken equal to 100
15 16	Chrysene, 30 g, hydrogenation to tetrahydrochrysene	0.0460	7.67	80
17	Tetrahydrochrysene, 30 g, hydrogenation to octahydrochrysene	0.0440	7.33	76
18	Benzene, 20 g	0.0382	6.37	100
19	Octahydrochrysene, 19.8 g, hydrogenation to dodecahydrochrysene	0.0367	6.12	96

TABLE 4

Relative Hydrogenation Rates of Condensed Aromatic Hydrocarbons and Their Hydro Derivatives

Exp. No.	Hydrogenation Reaction	Relative Rate With the Hydrogenation Rate of Benzene Taken Equal to 100		
		Catalysts and Hydrogenation Conditions		
		WS_2, 400°, 150 atm	MoS_2, 420° [7] 200 atm	Ni + Al_2O_3 [2] 120-202°, 30-50 atm
1	Naphthalene → tetralin	2300	1409	314
2	Tetralin → decalin	250	287	24
3	Anthracene → 9,10-dihydroanthracene	6187	–	326
4	9,10-Dihydroanthracene → tetrahydroanthracene	1295	–	308
5	Tetrahydroanthracene → octahydroanthracene	449	–	147
6	Octahydroanthracene → perhydroanthracene	291	–	4
7	Chrysene → tetrahydrochrysene	80	–	–
8	Tetrahydrochrysene → octahydrochrysene	76	–	–
9	Octahydrochrysene → dodecahydrochrysene	96	–	–

WS_2, of the formed dodecahydrochrysene, since the hydrogenation of the last benzene ring should proceed at a rate close to the hydrogenation rate of benzene [1].

Judging from the complexity of the chrysene hydrogenation products, being a multicomponent mixture, together with the described basic reaction course, it is also possible to have the simultaneous addition of hydrogen in two other directions, in particular the successive hydrogenation of rings 1 and 4, 1 and 2 and the simultaneous hydrogenation of rings 1 and 2. The probability of such reaction courses is demonstrated by the studies of Prokopets, Pavlenko and Boguslavskaya on the mechanism for the hydrogenation of tetrahydroanthracene [4] and also by the studies of Coulson [6]. The latter, who hydrogenated pyrene in the presence of MoOS, obtained a mixture of hydro derivatives ranging from the di- to the decahydropyrene.

If, on the one hand, the relative hydrogenation rates of naphthalene (2300) and its derivatives – tetrahydroanthracene (449) and octahydrochrysene (96) – are compared, with the hydrogenation rates of benzene (100) and its derivatives – tetralin (250) and octahydroanthracene (291) – on the other hand, then it can easily be seen that an essential difference exists in the nature of the influence exerted by increasing the complexity of the molecule structure on the hydrogenation rate in the presence of WS_2 for the two classses of aromatic hydrocarbons – condensed and noncondensed: for the first the hydrogenation rate drops sharply with increase in molecule sixe (the chemical character of the condensed aromatic rings remaining constant); for the second, saturating the benzene ring, the hydrogenation rate not only fails to decrease in measure with increase in the molecular weight of the compound (due to the accumulation of side saturated rings and chains), but it noticeably, and in some cases [1], strongly rises.

The influence of increased molecule complexity on the hydrogenation rate of condensed aromatic hydrocarbons is brought out very clearly on comparing the hydrogenation rates of naphthalene and chrysene. The latter, not differing from naphthalene in the character of its structure and, consequently, in the degree of unsaturation, is hydrogenated at a rate nearly 30 times slower than naphthalene.

Apparently, this is explained by the fact that the larger unsaturated molecules, first, simultaneously react with a large number of active catalyst centers and consequently the catalyst efficiency diminishes, and second, and this may have decisive significance, the higher moleculer weight hydrogenation products are desorbed with greater difficulty from the catalyst surface, which also reduces its efficiency. Here, apparently, it is necessary to seek a reason for the fact that with a certain degree of molecule complexity the hydrogenation rate of the aromatic condensed hydrocarbon becomes even less than the hydrogenation rate of benzene.

Different relationships are observed in the hydrogenation (in the presence of WS_2) of benzene and its derivatives: an increase in the size of the aromatic hydrocarbon molecule due to saturated condensed cycles (order: benzene → → tetralin → octahydroanthracene) or alkyl radicals [1] causes an increase in the hydrogenation rate. In order to explain these seemingly contradictory relationships it is necessary to take into consideration that: 1) condensed aromatic hydrocarbons from the nature of their unsaturated bonds are capable of adding hydrogen at a considerably faster rate than is the benzene ring; 2) for the catalytic addition of hydrogen to any unsaturated compound it is necessary for the latter to be in contact with the active catalyst centers for a definite length of time in the chemically sorbed state. The more difficult the compound is to hydrogenate, the longer, apparently, should be the time required for the chemosorption reaction. For rapidly reacting condensed aromatic hydrocarbons a prolonged chemosorption of the molecule being hydrogenated on the active catalyst centers and a slow desorption of the hydrogenation products retards the reaction course. The factors, causing the prolonged existence of the reacting substances and reaction products on the catalyzing surface, such as the strong adsorption and slow desorption conditioned by increasing molecule complexity, should favor a drop in the hydrogenation rate (in the case of chrysene and tetrahydroanthracene).

For single ring aromatic hydrocarbons that hydrogenate slowly it is necessary to have a longer chemosorption period on the catalyst. The great tendency of the molecule to be adsorbed on the catalyst surface, usually increasing with increase in molecule complexity, can create, in the case of difficultly hydrogenated compounds, more favorable conditions for reaction and, in the final analysis, can accelerate the reaction, especially if the hydrogenation products are quickly removed from the catalyst surface. For example, the duration of the benzene molecule in the adsorbed condition on the surface of a catalyst with relatively low activity may prove to be insufficient for hydrogenation. Increasing the complexity of the benzene molecule by introducing alkyl substituents or a saturated condensed cycle into the ring increases absorption of the aromatic hydrocarbon on the catalyst and in this way, under the same reaction conditions, creates more favorable possibilities for reaction of the aromatic hydrocarbon with hydrogen. However, in the case of hydrogenation in the presence of a highly active catalyst, the indicated increase in the complexity of the benzene molecule may not cause accelerated hydrogenation of the aromatic ring, since in this case a prolonged existence of the hydrocarbon molecule in the chemically sorbed state on the active centers of the catalyst is not necessary for achieving the addition of hydrogen to the benzene ring. Apparently, a similar phenomenon is also observed in the case of hydrogenating single ring aromatic hydrocarbons in the presence of the highly active catalyst MoS_2 at elevated temperature: benzene, toluene, m-xylene and pentamethylbenzene all add hydrogen at practically the same rate at 420° [7].

On lowering the hydrogenation temperature in the presence of highly active catalysts an increase in the complexity of the aromatic hydrocarbon can, in certain cases, create difficulties for bringing up the activated hydrogen atoms to the molecule being hydrogenated on the catalyst surface. A similar phenomenon was observed [8] in the hydrogenation of benzene and its methyl derivatives in the presence of $Ni + Al_2O_3$ at 120-200°. In the case of hydrogenation in the presence of MoS_2 at 240° it was also revealed that m-xylene adds hydrogen at a rate 1.3 times slower than benzene, while at elevated temperature (420°) the hydrogenation rates for benzene and m-xylene are the same.

From the practical viewpoint it is essential to mention that in the hydrogenation of fuel crudes, containing condensed aromatic hydrocarbons, in the presence of WS_2 and similar high temperature catalysts, a redutcion in the hydrogenation rate should be observed in measure with increase in the degree of hydrogenation and with increase in the boiling point (molecular weight) of the fractions being hydrogenated.

SUMMARY

The relative hydrogenation rates of the condensed aromatic hydrocarbons – naphthalene, anthracene, chrysene and their hydro derivatives – were measured in the presence of WS_2 catalyst, at 400°, and a pressure of 150 atm.

It was found that with the hydrogenation rate for benzene taken as 100, that the hydrogenation rates (in round numbers) are: naphthalene - 2300, anthracene - 6200, 9,10-dihydroanthracene -1300, tetrahydroanthracene - 450, octahydroanthracene - 290, chrysene - 80, and octahydrochrysene - 96.

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SULFONATION REACTION

XXXIV. Hydrolysis of Sulfonic Acids of the Benzene Series

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It is known that the sulfonic acid mixtures, formed in the low temperature sulfonations of toluene or phenol, contain a large amount of the o-sulfonic acid, which on elevating the temperature is converted in the reaction mixture into the para- isomer, due to the fact that the ortho- isomer is more easily hydrolyzed than the para- isomer. Hydrolysis of the unstable ortho- isomer and repeated sulfonation lead to a mixture rich in the para- isomer. Experiments on the hydrolysis of the sulfonic acid isomers of the benzene series were made by Obermiller [1], who heated the sodium salts of o-, p- and m-phenolsulfonic acids with excess hydrochloric acid on the water bath for 7 and 9 hours. These experiments revealed that the meta- isomer is completely resistant to hydrolysis, the para- isomer is hydrolyzed to the extent of 31-37 %, while the ortho- isomer is 97-99% hydrolyzed.

Vesely and Stojanova [2] in determining the hydrolysis temperatures of different sulfonic acids found that m-toluene-sulfonic acid begins to hydrolyze at 155°, the p- acid at 186°, and the o- acid at 188°. As a result, of the three isomers the meta- isomer is most easily hydrolyzed and the ortho- isomer is the most difficult. m-Chlorobenzenesulfonic ccid also begins to hydrolyze before (182°) its para- isomer (200°).

Consequently, according to the data of Obermiller, the kinetic stability of hydrolysis of the isomeric phenolsulfonic acids follows the order: m > p > o, and according to the data of Vesely and Stojanova, the stability to hydrolysis of the isomeric toluenesulfonic acids is in the order: o > p > m.

In the present paper we studied the influence of the position of different substituents in the benzene ring on the hydrolysis rate of sulfonic acids, the isomerization of the para- isomer of phenolsulfonic acids, and the hydrolysis of benzenepolysulfonic acids.

EXPERIMENTAL

For the study benzenesulfonic acids were chosen, containing the ring activation group I of type (−OH), the ring deactivation group I of type (−Cl), group II of type (−COOH) and the amino group, changing orientation in strongly acid medium.

To a weighed sample of the sulfonic acid in a test tube was added either hydrochloric or phosphoric acid in such amount and such concentration as would give about 4.5 moles of water per mole of sulfonic acid. The stoppered test tube was kept at a definite temperature, and then, after dissolving the mixture in water, the amount of hydrolyzed sulfonic acid was found from the amount of formed sulfuric acid, which was determined gravimetrically as barium sulfate.

The experimental results, given in Table 1, show that with any of the investigated substituents the kinetic stability to hydrolysis of isomeric sulfonic acids follows the order: m > p > o. Only in the case of the p- and m-sulfobenzoic acids were we unable to achieve a definite result.

And so the experiments revealed that m-phenolsulfonic acid is considerably more stable than the para- isomer. With the purpose of initiating experiments on the isomerization of these acids we determined at which temperatures noticeable hydrolysis of the para- isomer begins. In the literature Armstrong and Miller [3] have reported on the hydrolsyis of the para- isomer. They metnioned a temperature of 116° as denoting the beginning of hydrolysis for the acid. Later Bruckner [4] indicated that 123-125° was the hydrolysis temperature for p-phenolsulfonic acid. Our hydrolysis was carried out without mineral acid. The experimental results, given in Table 2, reveal that the para- isomer is noticeably hydrolyzed below 80°. Apparently, the mentioned authors indicated slightly high temperatures, due to the fact that they studied the hydrolysis in the presence of a large amount of water. Despite the fact that Experiments 276, 332 and 335 (Tables 1 and 2) were carried out under different conditions (at different temperatures, with hydrochloric acid or without it), almost the same result was obtained in all three cases — about 44% of the p-phenolsulfonic acid was hydrolyzed. This is explained as being due to the formation of evolved sulfuric acid in the reverse of the phenol sulfonation reaction, the concentration of which in Experiment 276 attains a value of 36.5 %.

TABLE 1

Exp. No.	Sulfonic Acid	Moles of water taken per mole of sulfonic acid	Mineral acid		Temperature	Time (in hours)	Amount of hydrolyzed sulfonic acid (in %)
			Nature	Concentration in the mixture (in %)			
332	p-Phenol-	4.68	HCl	16.9	101°	25	45.7
335	p-Phenol-	4.45	HCl	18.1	109.5	25	44.1
334	m-Phenol-	4.58	HCl	18.5	109.5	25	0.4
336	m-Phenol-	4.53	HCl	16.8	126	25	1.1
324	o-Chlorobenzene-	4.47	H_3PO_4	79.6	163	100	49.1
326	p-Chlorobenzene-	4.59	H_3PO_4	79.5	163	100	14.4
325	m-Chlorobenzene-	4.74	H_3PO_4	78.5	163	100	2.2
321	o-Chlorobenzene-	4.58	H_3PO_4	79.8	184	8	30.0
323	p- Clorobenzene-	4.63	H_3PO_4	79.4	184	8	7.7
322	m-Chlorobenzene-	4.74	H_3PO_4	79.3	184	8	1.9
315	o-Sulfobenzoic	4.49	H_3PO_4	52.9	185	12	7.6
314	p-Sulfobenzoic	4.51	H_3PO_4	55.5	185	12	0
316	m-Sulfobenzoic	4.51	H_3PO_4	55.3	185	12	0
308	Orthanilic	4.48	H_3PO_4	61.6	184	4	89.6
307	Sulfanilic	4.55	H_3PO_4	62.4	184	4	2.2
309	Metanilic	4.49	H_3PO_4	61.8	184	4	0
305	Orthanilic	4.50	H_3PO_4	61.6	211	4	89.8
304	Sulfanilic	4.50	H_3PO_4	62.4	211	4	66.2
306	Metanilic	4.51	H_3PO_4	61.8	211	4	0

TABLE 2

Hydrolysis of p-Phenolsulfonic Acid

Exp. No.	Moles of Water taken per mole of sulfonic acid	Temperature	Time (in hours)	Hydrolyzed (in %)
276	4.55	100°	25	43.5
280	4.34	79	25	3.5
277	4.47	66	25	0

TABLE 3

Action of Sulfuric Acid on Benzoic Acid for 8 Hours at 163°

Exp. No.	Sulfuric Acid concentration	Amount of reacted sulfuric acid (in % of amount taken)
285	99.6	17.4
289	94.7	13.5
291	88.6	3.4

TABLE 4

Hydrolysis of Benzene Di- and Trisulfonic Acids

Exp. No.	Sulfonic Acid	H_2SO_4 concentration in the mixture	Moles of water per mole of sulfonic acid	Temperature	Time (in hours)	Hydrolyzed (in %)
273	1,3-Benzenedi-	84.5	2.1	234°	8	11.8
272	1,3,5-Benzendi-	0	4.0	235	8	0
274	1,3,5-Benzenetri-	85.3	2.0	234	8	0
287	1,3,5-Benzenetri-	83.7	2.1	285	8	Oxidation

The following experiment revealed that even a lower concentration of sulfuric acid in the sulfonation mixture can sulfonate phenol. One gram of phenol and 1 g of 70% sulfuric acid was heated at 101.5° for 48 hours. Titration of the sulfonation mixture, dissolved in water, with 0.1 N alkali solution revealed that the concentration of sulfuric acid in the reaction product had dropped to 32%.

As a result, in three experiments on the hydrolysis of p-phenolsulfonic acid fairly rapid equilibrium is reached between phenol and the sulfonic acid on the one hand, and between the sulfonic acid and water on the other hand. However, this is a false equilirbium, for at the same time the process for the transformation of the less stable para-

isomer into the more stable meta- isomer is taking place. The transformation of the para- isomer into the meta- isomer proceeds very slowly at 100°.

We attempted to isomerize the p-phenolsulfonic acid in the presence of sulfuric acid at 163°. For this it was necessary to know the sulfuric acid concentration at which neither appreciable disulfonation occurs, nor the significant formation of phenol due to hydrolysis. In two experiments weighed samples of p-phenolsulfonic acid were heated at 163° for 8 and 25 hours with 62.8% (2.4 moles) and with 58.8% (2 moles) sulfuric acid. Titration with alkali revealed that in the first experiment the sulfuric acid concentration dropped to 61.6%, i.e., a slow disulfonation was taking place, while in the second experiment there was hardly any change (59.0%).

Making use of the obtained data, two experiments on the isomerization of p-phenolsulfonic acid were made in the following manner. A weighed sample of the p- acid was heated with 2.06 moles of 59.4% sulfuric acid per mole of sulfonic acid at 163° for 25 hours in a sealed tube. After dissolving in water, the mixture was analyzed by the method of gravimetrically determining the amount of sulfuric acid before and after bromination of part of the solution with bromide-bromate. Since in the bromination the sulfonic group is displaced from the para- isomer and not from the meta- isomer, then by difference, obtained by substracting the sulfuric acid, found after and before bromination, the amount of meta- isomer in the mixture was determined, in the first experiment being equal to 12.8% of the total amount of phenolsulfonic acids.

In the second experiment 2.09 moles of 60% sulfuric acid per mole of sulfonic acid was taken. Heating at 163° was continued for 150 hours. In the water solution there separated a black insoluble deposit, representing 3.7% of the sulfonic acid weight, and consequently it was filtered off before analysis. This introduced some error in the analysis result, which showed a m-phenolsulfonic acid content of 39.3%.

These experiments revealed that there exists not only transformation of o-phenolsulfonic acid into the para- isomer on raising the temperature, but also that the latter is transformed, to be sure, much more slowly into the m-sulfonic acid, being the isomer most stable to hydrolysis.

The experiments further revealed (Table 1) that the sulfobenzoic acids are extremely stable to hydrolysis. Since sulfuric acid [5] facilitates the hydrolysis, experiments were set up in its presence. A preliminary study of the action of sulfuric acid on benzoic acid revealed (Table 3) that 88% sulfuric acid at 163% still sulfonates benzoic acid; consequently, to exclude the sulfonation process, all three of the sulfobenzoic acid isomers were heated with 70% sulfuric acid for 12 and 75 hours at 163°. However, not one of the isomers suffered hydrolysis. The p-sulfobenzoic acid also fails to be appreciably hydrolyzed at 233° for 4 hours with 82% phosphoric acid.

The sulfonic acids of aniline hydrolyze with greater ease, as is shown by the experimental results presented in Table 1. Only the metanilic acid failed to be hydrolyzed, while the orthanilic acid is hydrolyzed even at 163° (25% in 12 hours).

Finally, the benzenedi- and trisulfonic acids were subjected to hydrolysis. The experimental results, presented in Table 4, reveal that benzenetrisulfonic acid fails to lend itself to hydrolysis. On opening the sealed tube (Experiment 287) the presence of gas pressure in the tube was revealed, the solution of the mixture in water was colored brown, and the gravimetric determination of the amount of sulfuric acid revealed a decrease instead of an increase. The sulfuric acid was lost in oxidation.

Friedel and Crafts [6] indicate that benzenedisulfonic acid begins to hydrolyze in phosphoric acid only at 300°. The indicated temperature is slightly high, and the hydrolysis of benzenedisulfonic acid can proceed at a considerably lower temperature as is seen from the data in Table 4.

PREPARATIVE PART

p-Phenolsulfonic acid was identified as the benzylisothiourea salt melting at 167°. Recrystallization failed to raise the melting point. The free p-phenolsulfonic acid fails to hydrolyze when its dilute aqueous solution is boiled for 0.5 hour in the presence of small quantities of hydrochloric acid (i.e., under the conditions of precipitating the sulfuric acid with barium chloride).

m-Phenolsulfonic acid was obtained from thrice recrystallized metanilic acid, identified as the benzylisothiourea salt with m.p. 145°.

Metanilic acid was diazotized with amyl nitrite in glacial acetic acid in the presence of excess concentrated hydrochloric acid. The solution was diluted with water, heated at 70° to termination of nitrogen evolution the amyl alcohol was extracted with benzene, and the filtered solution was evaporated in vacuo at 65° A test sample of the obtained m-phenolsulfonic acid was heated in a dilute solution with bromide bromate and HCl at 50° for 1 hour. Here the absence of a precipitate indicated the absence of either the ortho- or para- isomer.

The obtained p- and m-phenolsulfonic acids contained water, the amount of which was established by titrating a weighed sample with 0.1 N alkali, and by titrating with bromide-bromate solution in the cold. The results by the two methods differed by 0.5-1%. Also determined was the amount of sulfuric acid, evolved from the p- siomer in its bromination at 50°. The yield of barium sulfate was 99% of the expected.

o-Chlorobenzenesulfonic acid was obtained from orthanilic acid by the Sandmeyer reaction. Its salt was converted into the sulfonyl chloride, and then into the free acid. The amide, obtained from the chloride without recrystallization, had m.p. 182-185°.

m-Chlorobenzenesulfonic acid was obtained in a similar manner from metanilic acid. The amide had m.p. 144°.

o-Sulfobenzoic acid with m.p. 67.5° was obtained from anthranilic acid through the dithiosalicylic acid [7].

The remaining sulfonic acids were obtained either by the purification of technical products or by methods that are excellently described in the chemical literature.

SUMMARY

1. It was found that the hydrolysis of monosubstituted sulfonic acids of the benzene series, for the four investigated substituents ($-OH$, $-Cl$, $-COOH$, $-NH_2$), proceeds at a different rate depending on the position of the substituent. In all cases the kinetic stability of the isomers to hydrolysis follows the order: m > p > o.

2. The ability of p-phenolsulfonic acid to isomerize into the meta- isomer at 163° was shown.

3. The hydrolysis conditions for some of the sulfonic acids of the benzene series were shown.

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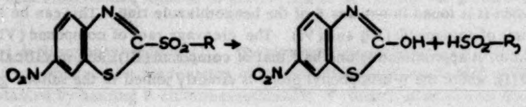
HYDROLYTIC CLEAVAGE OF ARYL AND ALKYL 2-BENZOTHIAZOLYL SULFONES

II. INFLUENCE OF CERTAIN SUBSTITUTENTS ON THE RELATIVE CLEAVAGE RATE

I. A. Alekseeva and I. Ya. Postovsky

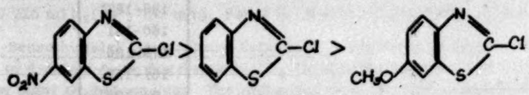
It was recently shown by us that aryl and alkyl 6-nitro-2-benzothiazolyl sulfones readily suffer hydrolytic cleavage under the influence of dilute acids and alkalis [1]. Thus, the cleavage of 6-nitro-2-benzothiazolyl 4-nitrophenyl sulfone gives 6-nitro-2-hydroxybenzothiazole (6-nitro-2-benzothiazolinone) and p-nitrobenzenesulfinic acid, i.e., the cleavage proceeds by the scheme:



where R = $O_2NC_6H_4$.

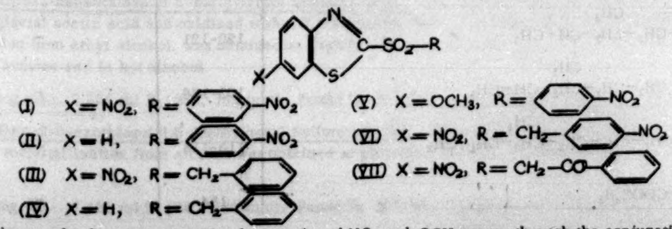
We assume that the cleavage for sulfones with other residues also proceeds in accord with this scheme.

It could be assumed that a substituent in position 6 will exert its influence on the stability of the substance as regards the hydrolytic agent. If the electron acceptor NO_2 group in position 6 will facilitate this cleavage, then the electron donor CH_3O group in the same position should retard this reaction. The opposite character of the influence of the NO_2 and CH_3O groups in position 6 of the benzothiazole ring through the conjugation chain at meso-carbon 2 (–N=C– groups) can also be observed when a comparison is made of the reactivity of 2-chlorobenzothiazole versus that of 6-nitro-2-chloro- and 6-methoxy-2-chlorobenzothiazoles:



It was found that the reaction of these chlorides with the sodium salt of p-nitrothiophenol proceeds at different rates, in which connection the reactivity of the chlorine atom drops sharply from 6-nitro-2-chlorobenzothiazole to 6-methoxy-2-chlorobenzothiazole.

To establish the influence of the NO_2 and OCH_3 groups on the relative stability of the corresponding sulfones to hydrolysis, a comparison was made of the cleavage rates of compounds (I-VII) under identical conditions:



The degree of influence exerted by the mentioned NO_2 and OCH_3 groups through the conjugation chain on the bond undergoing rupture can be approximately judged by the yield of the 2-benzo-thiazolinone, obtained as the result of cleavage under the same periods of time. The accuracy of these determinations was ± 1%. To determine the degree of cleavage with greater accuracy, using more exact analysis methods so as to be able to obtain the reaction rate constants, proved impossible. However, the investigation method used in this study was fully sufficient to permit judging as to the relative stability of the different compounds with respect to hydrolysis.

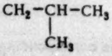
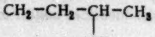
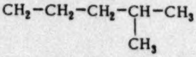
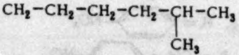
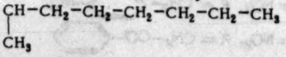
It was found that the cleavage of the nitro compound (I) when heated in alkaline medium on the water bath at 94° for 10 minutes was 92%, based on the isolated 6-nitro-2-benzothiazolinone. At the same time the cleavage of compound (II), not containing the NO_2 group, was roughly only 3%. A similar influence of the nitro group was also observed when the cleavage rates of compounds (III) and (IV) were compared. In alkaline medium the nitro compound (III) is completely cleaved when heated on the water bath at 94° for 60 minutes, while under the same conditions the cleavage of the compound without the NO_2 group (IV) is only 60%. In acid medium, in which the benzothiazole sulfones in general are cleaved with greater difficulty than in alkaline medium, the cleavage of substance (III) was 58% when heated for 5 hours (bath temperature 110°), while compound (IV) under the same conditions was cleaved a total of only 3%.

As regards compound (V), containing the electron donor methoxy group in position 6, then it, actually, proved to be extremely stable and practically failed to change when heated for many hours (up to 14 hours) in acid and alkaline media at 94 and 110°.

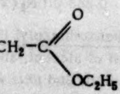
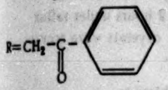
It is interesting to note that the nitro group, found in the radical R (in the p-position), exerts an influence that is oppsoite to that shown when it is found in position 6 of the benzothiazole ring. This can be seen from a comparison of the relative cleavage rates of compounds (III) and (VI). The cleavage rate of compound (VI) at 110°, when heated for 5 hours in acid medium, is approximately one half that of compound (III), and specifically it is 32%. Under these conditions compound (I), where the p-nitrophenyl group is directly joined to the sulfone group, is cleaved even slower (17%).

Not only a substituent in position 6 but also the radical R should exert an influence on the stability of sulfones to hydrolysis.

We studied the cleavage of alkyl 6-nitro-2-benzothiazolyl sulfones, where R is an aliphatic residue with a straight chain from C_1 to C_7[compounds (VIII-XIV)] and of some sulfones that contained side methyl groups in the chain [compounds(XV-XIX)]. The data on these compounds are given in the Table.

Compound Number	Value of R in alkyl 6-nitro-2-benzothiazolyl sulfones	Melting point	
		Found	Indicated in the literature [2]
(VIII)	CH_3	186-187°	186°
(IX)	C_2H_5	160-161	160
(X)	C_3H_7 -n	179-180	181
(XI)	C_4H_9 -n	151-152	152
(XII)	C_5H_{11}-n	124-125	125
(XIII)	C_6H_{13}-n	112-113	111.5
(XIV)	C_7H_{15} -n	123-124	123.5
(XV)	 $CH_2-CH(CH_3)-CH_3$	122-123	124
(XVI)	 $CH_2-CH_2-CH(CH_3)-CH_3$	112-113	115
(XVII)	 $CH_2-CH_2-CH_2-CH(CH_3)-CH_3$	120-121	–
(XVIII)	 $CH_2-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$	135-136	–
(XIX)	 $CH(CH_3)-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	115-116	–
(XX)	$CH_2-COOC_2H_5$	134	–

It was found that the cleavage rate is significantly retarded with increase in chain length; thus, for example, if sulfone (VIII), where R = CH_3, is 90% cleaved when heated in acid medium at 94° for 60 minutes, then sulfone (XII), where R = C_5H_{11}, is cleaved a total of only 17%, while sulfone (XIV), where R = C_7H_{15}, is not cleaved at all (however, its cleavage to the extent of 96% was achieved by heating in an alkaline medium for 20 minutes at 94°; with R = CH_3 the cleavage under the same conditions and for the same length of time is already complete at 60°).

Expecially noteworthy is the ease of cleavage of compounds (XX), where R =CH₂−C  $R = CH_2-C(=O)OC_2H_5$, and (VII), where  $R=CH_2-C(=O)-C_6H_5$, i.e., compounds in which a carbonyl group is found in the beta-position to the sulfone group. In these compounds cleavage in alkaline medium already proceeds in a matter of several minutes with slight heating (up to 40°). Apparently, here the cleavage also proceeds at the linkages of the methylene group with the sulfone and carbonyl groups, similar to the situation that exists in the hydrolytic cleavage of 1,3-diketones.

EXPERIMENTAL*

The sulfides used for the synthesis of the sulfones were obtained by reacting the corresponding alkyl halides with mercaptobenzothiazole, using the method described in [2]. The sulfones were obtained from the sulfides in yields of 80-85% by the oxidation with 7.5% $KMnO_4$ solution in glacial acetic acid, using the method described in the literature [1,2].

1. 2-Benzothiazolyl 4-Nitrophenyl Sulfone (II). The starting 2-benzothiazolyl 4-nitrophenyl sulfide is described in the literature [3]; it was obtained by the reaction of 2-mercaptobenzothiazole with p-chloronitrobenzene. This sulfide is more readily obtained by heating 2-chlorobenzothiazole in alcohol solution with the sodium salt of p-nitrothiophenol.

Two grams of 2-chlorobenzothiazole was dissolved in 50 ml of ethyl alcohol. To this solution was added a solution of 2 g of p-nitrothiophenol in 50 ml of alcohol and 60 ml of 2 N NaOH. After heating for 2.5 hours and subsequent cooling there separated yellow platelets from the reaction mixture. Yield 1.20 g (34%). M.p.112-113° (literature 111.5-112.5° [3]). Oxidation with 7.5% $KMnO_4$ solution gave the sulfone with m.p. 213-214° (literature 207-208° [3]) in 90% yield.

2. 2-Benzothiazolyl Benzyl Sulfone (IV). The sulfone was obtained in 65% of the theoretical yield by the oxidation of the sulfide, described earlier [4]. After recrystallization from dilute alcohol the sulfone was obtained as glistening colorless platelets with m.p. 105-106°.

5.100 mg sub.: 0.225 ml N_2 (24°, 732 mm). Found %: N 4.88. $C_{14}H_{11}O_2NS_2$. Calculated %: N 4.84.

3. 6-Methoxy-2-Benzothiazolyl 4'-Nitrophenyl Sulfone (V). The corresponding, not known, sulfide was obtained by the condensation of 2-chloro-6-methoxybenzothiazole [5] with the sodium salt of p-nitrothiophenol with the addition of KI in boiling butyl alcohol medium. The sulfide had m.p. 128-130°. Yield 28%. The sulfone, obtained in 82% yield by the oxidation of the sulfide, after recrystallization from butyl alcohol had m.p. 247-248°.

The sulfone is soluble in hot butyl alcohol, readily soluble in acetone, and difficultly soluble in alcohol.

4.235 mg sub.: 0.318 ml N_2 (27°, 738 mm). 4.130 mg sub.: 0.314 ml N_2 (28°, 739 mm). 0.0352 g sub.: 6.057 ml 0.1 N $Na_2S_2O_3$. Found %: N 8.29, 8.39; OCH_3 8.89. $C_{14}H_7O_4N_2S_2(OCH_3)$. Calculated %: N 7.89; OCH_3 8.86.

4. 6-Nitro-2-Benzothiazolyl 4'-Methylamyl Sulfone (XVII). The corresponding sulfide with m.p. 45-49° was dissolved in glacial acetic acid and oxidized with a 7.5% aqueous $KMnO_4$ solution. The sulfone from the reaction, after recrystallization from ethyl alcohol, was obtained as slightly yellow needles with m.p. 120-121°. The sulfone is readily soluble in acetone and in hot alcohol.

3.140 mg sub.: 0.255 ml N_2 (26°, 732 mm). Found %: N 8.92. $C_{13}H_{16}O_4N_2S_2$. Calculated %: N 8.52.

5. 6-Nitro-2-Benzothiazolyl 5'-Methylhexyl Sulfone (XVIII). The sulfone, obtained by the oxidation of the oily sulfide, after recrystallization from alcohol was obtained as glistening colorless transparent leaflets, melting at 135-136°.

5.970 mg sub.: 0.421 ml N_2 (24°, 736 mm). Found %: N 7.85. $C_{14}H_{18}O_4N_2S_2$. Calculated %: N 8.17.

6. 6-Nitro-2-Benzothiazolyl 1'-Methylheptyl Sulfone (XIX). The sulfide with m.p. 107° was oxidized with permanganate to the sulfone in 75% yield. After recrystallization from alcohol the sulfone was obtained as silky, slightly

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* Preparation directions are only given for the sulfones that are not described in the literature. Compounds (I, III, VI, VII) were described earlier [1].

yellow needles with m.p. 115-116°.

4.955 mg sub.: 0.343 ml N_2 (25°, 730 mm). Found %: N 7.62. $C_{15}H_{20}O_4N_2S_2$. Calculated %: N 7.86.

7. 6-Nitro-2-Benzothiazolyl Propionyloxymethyl Sulfone (XX). 6-Nitro-2-mercaptobenzothiazole (2.65 g) was dissolved in 25 ml of alcohol, and to this solutuion was added 6.3 ml of 2 N NaOH and 1.6 g of KI. The mixture was brought to a boil, and to it was added 5.5 ml of ethyl chloroacetate. After heating for 2 hours under reflux the mixture was poured into ice water. The initially obtained oil crystallized on standing. The crystals were recrystallized from methyl alcohol. Yellow needles, m.p. 97°. Yield 1.95 g (54%).

The sulfide is readily soluble in methyl and ethyl alcohols, acetone and hot carbon tetrachloride.

4.690 mg sub.: 0.375 ml N_2 (21°, 748 mm). 5.500 mg sub.: 0.459 ml N_2 (21°, 748 mm). Found %: N 9.14, 9.54. $C_{11}H_{10}O_4N_2S_2$. Calculated %: N 9.39.

Oxidation of the sulfide with $KMnO_4$ gave the sulfone. After recrystallization from alcohol the sulfone was obtained as slender colorless needles with m.p. 134° and in 60% yield. The sulfone is soluble in hot methyl and ethyl alcohols, and is extremely soluble in acetone.

5.025 mg sub.: 0.382 ml N_2 (21°, 744 mm). 4.990 mg sub.: 0.363 ml N_2 (22°, 744 mm). Found %: N 8.64, 8.39. $C_{11}H_{10}O_6N_2S_2$. Calculated %: N 8.49.

SUMMARY

1. It was shown that the electron acceptor nitro group in aryl 6-nitro-2-benzothiazolyl sulfones (I, III) lowers the stability of the sulfone toward hydrolysis (in both acid and alkaline media), while, in contrast, the electron donor methoxy group in the aryl 6-methoxy- sulfone (V) raises it significantly.

2. The relative hydrolytic cleavage rate for sulfones with aliphatic radicals steadily diminishes with increasing chain length in going from the lower to the higher members of a homologous series.

3. Several new aryl and alkyl benzothiazolyl sulfones are described in this study.

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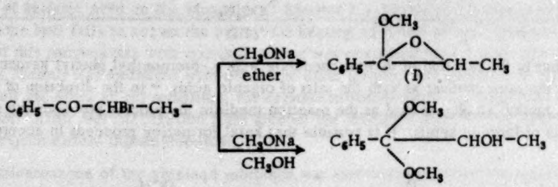
ANOMALOUS REACTIONS OF α-BROMO KETONES

IV. Reaction of Sodium Phenolate with α-Bromoethyl Phenyl Ketone

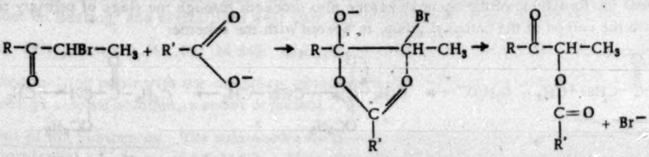
T. Temnikova and S. Myukhyurdari

Apparently, in the action of nucleophilic reagents on α-bromo ketones, in particular the sodium alcoholates and the salts of organic acids, the reagent in all cases first reacts with the carbon atom of the carbonyl group in the bromo ketone [1]. However, the structure of the final reaction products depends on the process conditions and on the nature of the operating reagent.

The action of sodium methylate on the α-bromoalkyl phenyl ketones in anhydrous ether gives the α-methoxy oxides (I) [2]; if methyl alcohol is used as the reaction medium the dimethyl ketals of the keto alcohols are obtained, formed as the result of the methoxy oxides reacting with the solvent [3].



On the other hand, the reaction of α-bromo ketones with the salts of organic acids results in the formation of keto alcohol esters, corresponding to the bromo ketone; only in rare cases in these reactions is the formation of esters, corresponding to the isomeric keto alcohol, observed, which points to the probability in these cases that the anions of the acids first react with the carbonyl group of the bromo ketone. It is very probable that also in normal substitution reactions the first stage of the reaction is that of the acid anion with the carbon of the carbonyl group, with subsequent rearrangement of the molecule in the cleavage of the bromide ion, in accord with the scheme:



Analogous intermediate products were assumed earlier many times for explaining the intramolecular migrations of acyl groups [4], and also for explaining the formation of isomeric keto alcohols in the methanolysis of keto alcohol esters [5].

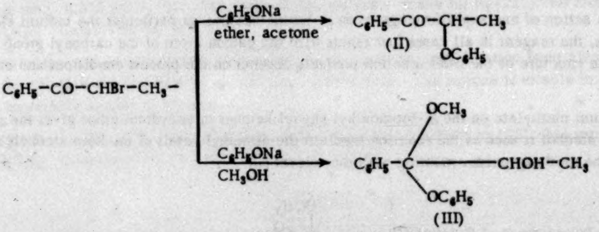
It appeared of interest to study the reaction between sodium phenolate and the α-bromo ketones under different conditions, since phenol, as a nucleophilic reagent, is weaker than the alcohols and stronger than the acids; on the other hand, in contrast to the acids, phenol does not contain two oxygen atoms and, in the case of primary formation of the addition product, the latter cannot undergo intramolecular transformation in accord with the scheme proposed for the addition products of acid anions.

In the literature only several examples of the reaction of bromo ketones with sodium phenolate are described [6]; in all cases α-phenoxy ketones are obtained, the structures of which were not specially proven.

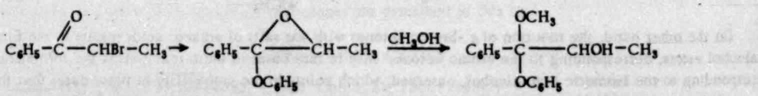
In the present work we studied the reaction between sodium phenolate and α-bromoethyl phenyl ketone in anhydrous ether and in methyl alcohol. It was found that the direction of the reaction depends on the solvent. It was observed that basically tar formation results when the reaction is carried out in anhydrous ether, and only in insignificant amount was it possible to isolate the α-phenoxy ketone, obtained earlier by Bradsher and Rosner [7] in the reaction of these same compounds in acetone solution. The structure of the phenoxy ketone as being a derivative of methylbenzoylcarbinol was proved by way of determining its ultraviolet absorption spectrum: the curve had two maxima, characteristic for the benzoyl grouping at λ272 and 328 mμ. Further proof of the structure was made by way of converting the compound into the monophenyl ether of 1,1-diphenyl-1,2-propanediol with m.p. 134°, obtained earlier by Stoermer and Riebel from the methyl ester of phenoxypropionic acid and phenylmagnesium bromide [8].

When the reaction between sodium phenolate and α-bromoethyl phenyl ketone was carried out in methyl alcohol a different reaction product was obtained – the ketal of methylbenzoylcarbinol (α-methoxy-α-phenoxybenzylmethylcarbinol) (III).

The structure of the latter was proved by its hydrolysis to methylbenzoylcarbinol.

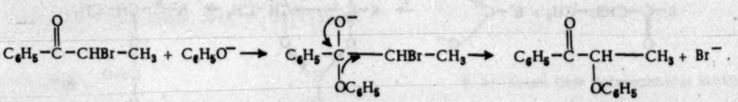


As a result, it was shown that in the reaction of sodium phenolate with α-bromoethyl phenyl ketone, in ether solution the reaction proceeds in the same manner as with the salts of organic acids, – in the direction of forming the ethers of the keto alcohol; when methyl alcohol is used as the reaction medium the process proceeds the same as with the alcoholates, – in the direction of forming ketals. It is possible that ketal formation proceeds in accord with the following scheme:



In connection with this it appeared of interest to study the reaction of the methyl lactolide of methylbenzoylcarbinol (I) with phenol. The reaction was run in benzene, and here the only product isolated was the ketal (III).

It is possible that the formation of the phenoxy ketone also proceeds through the stage of primary reaction of the phenolate ion with the carbon of the carbonyl group, in accord with the scheme:



EXPERIMENTAL

Action of Sodium Phenolate on α-Bromoethyl Phenyl Ketone

a) In Diethyl Ether Medium. To the dry sodium phenolate, prepared from 12 g of metallic sodium and suspended in dry ether, was slowly added with constant stirring an ether solution of 30 g of α-bromoethyl phenyl ketone. On conclusion of reaction the excess sodium phenolate and formed sodium bromide were filtered, while the ether was distilled off; the residue was a heavy dark brown tar. An attempt to isolate the substance by vacuum distillation only led to pronounced swelling. We were able to extract the reaction product by heating it with petroleum ether, in which the tar proved to be almost insoluble. Cooling of the extract gave colorless crystals, which were repeatedly recrystallized from petroleum ether. Yield 2.5 g, m.p. 76°.

Found %: C 79.40, 79.38; H 6.14, 6.10. M 220.9. $C_{15}H_{14}O_2$. Calculated %: C 79.62; H 6.19. M 226.

b) In Methyl Alcohol Medium. To a solution of sodium phenolate, prepared by dissolving 5 g of sodium in methyl alcohol with the subsequent addition of 21 g of phenol, was added 10 g of α-bromoethyl phenyl ketone, and the solution was heated with constant stirring to complete reaction. The sodium bromide precipitate was filtered, from the filtrate the alcohol was distilled off on the water bath, the residual oil was extracted with ether, and the ether solution was washed with water and alkali. After distilling off the ether the residual solid reaction product was recrystallized from petroleum ether. Colorless crystals with m.p. 124° were obtained.

0.1092 g sub.: 0.2970 g CO_2: 0.0700 g H_2O. 0.1056 g sub.: 0.2870 g CO_2; 0.0680 g H_2O. 0.0318 g sub.: 7.83 ml 0.1 N $Na_2S_2O_3$. 0.0380 g sub.: 9.1 ml 0.1 N $Na_2S_2O_3$. 0.0528 g sub.: 5 ml CH_4 (14°, 748 mm). 0.0516 g sub.: 5.1 ml CH_4 (14°, 748 mm). 0.1395 g sub.: 18.28 g benzene: Δt 0.155°. Found %: C 74.23, 74.14; H 7.17, 7.20; OCH_3 12.7, 12.1; act.H 1.00, 1.02. M 251. $C_{16}H_{18}O_3$. Calculated %: C 74.41; H 6.97; OCH_3 12.0; act.H 1. M 258.

Preparation of the Monophenyl Ether of 1,1-Diphenyl-1,2-Propanediol

To a solution of phenylmagnesium bromide, prepared from 4 g of Mg and 18 ml of bromobenzene, was added an ether solution of 3 g of phenoxypropionphenone. After decomposing the organomagnesium complex with water and distilling off the ether from the ether extract the residue was subjected to steam distillation for the purpose of removing benzene, bromobenzene and diphenyl. The substance, which congealed on cooling, was dried and recrystallized from ethyl alcohol. M.p. 133-134°, yield 3.6 g.

The substance is difficultly soluble in hot alcohol, poorly soluble in petroleum ether, and relatively soluble in benzene.

Found %: C 83.27; H 6.20; act.H 0.98. $C_{21}H_{20}O_2$. Calculated %: C 83.16; H 6.27; act.H 1.

Action of Sulfuric Acid on the Monophenyl Ether of 1,1-Diphenyl-1,2-propanediol. Dilute sulfuric acid even on heating to the boil fails to act on the ether. On heating with 60% sulfuric acid nearly to the boil the substance melted; heating at this temperature with constant stirring was continued for 2 hours. The reaction product (an oil with a strong odor of phenol) was extracted with ether, the ether solution was washed with alkali, and dried over Na_2SO_4. After distilling off the ether an oil remained, the crystallization of which we were able to achieve by the addition of 1 ml of alcohol. After recrystallization from alcohol the substance melted at 58° and failed to show a depression when mixed with unsymmetrical diphenylacetone.

The semicarbazone of the obtained substance was identical with the semicarbazone of unsymmetrical diphenylacetone (m.p. 167-169°), the mixed melting point was the same.

Action of Phenol on the Methyl Lactolide of Methylbenzoylcarbinol

To the freshly prepared methyl lactolide of methylbenzoylcarbinol (α-methoxy-α-phenyl-β-methylethylene oxide) with b.p. 62-64° at 2-2.5 mm, diluted with a double volume of dry benzene, was added a benzene solution of phenol (7 g of phenol for 7 g of oxide). The solution was allowed to stand overnight at room temperature. Colorless crystals were obtained from the reaction, yield 6.2 g. The substance is readily soluble in ether and chloroform, in benzene and alcohol on heating, and crystallizes well from petroleum ether. M.p. 123-124°.

Found %: OCH_3 12.0; act. H 1.09. M 249. $C_{16}H_{18}O_3$. Calculated %: OCH_3 12.0; act. H 1. M 258.

The mixed melting point with the substance, obtained by the action of sodium phenolate on α-bromoethyl phenyl ketone in methyl alcohol solution, was not depressed.

Hydrolysis of the Substances. The substances (4.5 g) were added gradually and with vigorous stirring to a solution of 50 ml of alcohol and 20 ml of 5% H_2SO_4. After complete solution of the substances the alcohol was removed by vacuum distillation, water was added to the residual substance and the reaction product was extracted with ether; from the ether solution the phenol formed as the result of hydrolysis was extracted by washing with alkali and then identified as the triiodophenol with m.p. 157-158°. The substance remaining in the ether solution was identified as methylbenzoylcarbinol by converting it with the aid of phenylmagnesium bromide into the glycol – 1,1-diphenyl-1,2-propanediol with m.p. 94°; the mixed melting point with the authentic glycol failed to show a depression.

SUMMARY

1. The reaction of α-bromoethyl phenyl ketone with sodium phenolate in diethyl ether medium gave α-phenoxyethyl phenyl ketone; the same reactants in methyl alcohol medium gave the mixed ketal of methylbenzoylcarbinol – α-methoxy-α-phenoxybenzylmethylcarbinol.

2. The action of phenol on the methyl lactolide of methylbenzoylcarbinol gave the ketal of methylbenzoylcarbinol – α-methoxy-α-phenoxybenzylmethylcarbinol.

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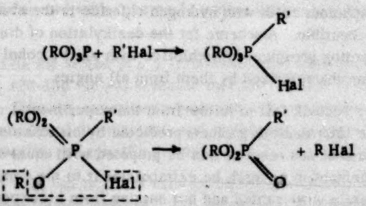
MECHANISM OF THE ARBUZOV REARRANGEMENT REACTION OF α,β-DIBROMODIETHYL ETHER WITH PHOSPHITES

V. S. Abramov and G. A. Karp

In 1905 Arbuzov [1] discovered a remarkable reaction for the conversion of phosphorous acid esters, under the influence of alkyl halides, into the esters of alkylphosphinic acids. The following scheme was given for the reaction:



Arbuzov's scheme is supported by the reaction for the action of alkyl halides on the esters of phosphorous acid, the alkyl radicals of which are different. As a result the ester of an alkylphosphinic acid is obtained, the alkyl radical of which corresponds to the alkyl halide taken. Also in support of the scheme is the addition product of methyl iodide to the phenyl ester of phosphorous acid, obtained by Michaelis and Kaehne [2] and decomposed by Arbuzov in accord with the scheme. For more than fifty years the addition product of methyl iodide to triphenyl phosphite has been the solitary example supporting the formation of monoacid halo-esters of orthophosphinic acids.

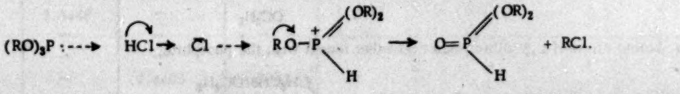
Arbuzov and Nesterov [3] obtained a number of crystalline products by the addition of alkyl iodides to triphenyl phosphite and studied the isomerization rate of phosphorous acid esters as a function of the size and structure of the radicals. The obtained results support the conclusions made earlier by Arbuzov that the Arbuzov reaction proceeds in two stages [4].

The kinetics for the isomerization of phosphorous acid esters was investigated by Staronka [5], who found that this process is autocatalytic.

Rumpf [6] believes that the isomerization reaction can proceed in the absence of alkyl halides by the following chain sequence:

$$2P(OR)_3 \rightarrow \overset{+}{R}P(OR)_3 + P(OR)_2\bar{O}$$
$$\overset{+}{R}P(OR)_3 + P(OR)_3 \rightarrow \overset{+}{R}P(OR)_2\bar{O} + \overset{+}{R}P(OR)_3,\ \text{etc.}$$

It was shown by Gerrard and Green [7] that as the result of reacting hydrogen chloride, ethyl iodide and acetyl chloride with tri-2-octyl phosphite, prepared from (+)-2-octanol, the corresponding inverted (−)-2-chloro and (−)-2-iodooctanes are obtained. A Walden inversion takes place in the process of transforming the phosphites. On this basis they proposed the following scheme for explaining the mechanism of the reaction:



Pudovik [8] studied the action of phosphorous trichloride on primary and secondary ethoxypentenols and butenols and obtained a definite proportion of the corresponding primary and secondary chlorides, from both the primary and secondary alcohols. The obtained results differed from those obtained in the action of hydrogen chloride on the ethoxypentenols and butenols. In the opinion of the author, the latter reaction proceeds with allylic rearrangement. Taking into consideration the different results of these reactions and the fact that up to now the addition products of alkyl halides with aliphatic phosphites had not been obtained, Pudovik believes it possible to give an explanation for the mechanism of the Arbuzov rearrangement, for which he postulates: in the reaction of phosphorous trichloride with ethoxypentenols and butenols the allyl rearrangement is absent, that this reaction proceeds through the formation of phosphites, and that the subsequent formation of halo derivatives proceeds through the Arbuzov reaction. However, neither phosphites, nor diallylphosphorous acids, nor any other substances, containing phosphorus, were isolated. In addition, the phosphorus containing part of the reaction does not figure in the experiment.

The proposed explanation for the mechanism of the Arbuzov reaction agrees with that offered by Gerrard [7]. Together with the inverted halo derivatives, Gerrard also obtained the esters of alkylphosphinic acids or dialkylphosphorous acids, which dealkylated very slowly due to the absence of a solitary pair of electrons for the phosphorous. Such behavior for these compounds ensues from the numerous investigations made by Arbuzov [1,9], who assigns the dialkylphosphorous acids as having pentavalent phosphorous in their structure.

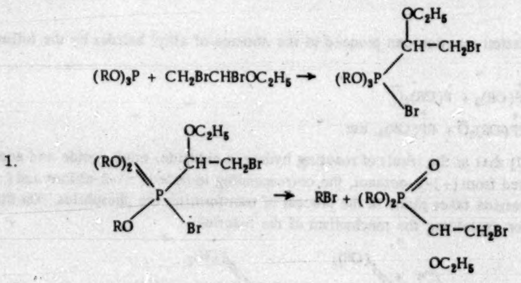
The diallylphosphorous acids were not obtained in Pudovik's experiments. This circumstance is explained by a new assumption that the diallylphosphorous acids are much more reactive then the dialkylphosphorous acids, although the reason for the easy reaction of the diallylphosphorous acids with hydrogen chloride in the absence of a solitary pair of electrons for the phosphorous remains incomprehensible. A scheme for the dealkylation of diallyphosphorous acids was not given. Kamai and Shugurova [10], in reacting phosphorous trichloride with allyl alcohol under ordinary conditions, obtained diallylphosphorous acid, which was characterized by them from all angles.

In our opinion [11] the conclusions made by Pudovik fail to follow from the experimental material presented by him, but instead are purely speculative, since the intermediate products predicted by his scheme are not confirmed. Apparently, other methods for explaining the course of this reaction can be proposed with equal success. Pudovik expands this particular case to the Arbuzov rearrangement in general; he extrapolates it to the completely unstudied tertiary phosphites [12], which to us appears completely unwarranted and not ensuing from his experiments.

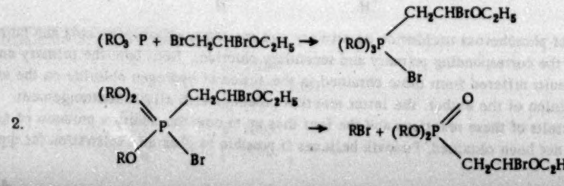
In the present study it was shown that the Arbuzov rearrangement for also the aliphatic phosphites proceeds with the formation of an intermediate addition product, i.e., it proceeds in two different independent stages. Although the addition product was not isolated chemically pure, still conclusive evidence of its formation was demonstrated by a series of indirect observations. This first noted instance of separate progress for both stages of the Arbuzov reaction for aliphatic phosphites is of interest for the reason that Atbuzov [1] believed that the addition products were "incapable of existence", while Kosolapoff [13] states that "they decompose spontaneously, and it is necessary to distill only the mixture of obtained final products".

Arbuzov and Grechkin [14] were able to isolate the addition product of methyltin triiodide with triethyl phosphite.

We studied the action of α,β-dibromodiethyl ether on phosphites. In theory the reaction can proceed in three possible directions:

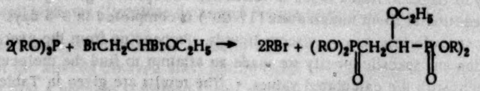


where the α-bromo atom of α,β-dibromodiethyl ether reacts with the phosphite.



where the β-bromo atom of α,β-dibromodiethyl ether reacts with the phosphite.

3.



$$2(RO)_3P + BrCH_2CHBrOC_2H_5 \rightarrow 2RBr + (RO)_2\underset{\underset{O}{\|}}{P}CH_2\overset{\overset{OC_2H_5}{|}}{C}H-\underset{\underset{O}{\|}}{P}(OR)_2$$

where both of the bromine atoms of α,β-dibromodiethyl ether react with the phosphite.

For the reaction the reactants were taken in equimolar amounts, for which reason we could hardly expect the reaction to take place in accord with scheme 3.

On the basis of the studies made [15] on the synthesis of hydrocarbons with the aid of α,β-dibromodiethyl ether, where it was shown that the latter reacts with organomagnesium compounds at the α-bromo atom, which appears to be the more active, we assumed that with phosphites also the α,β-dibromodiethyl ether reacts at the α-bromo atom, i.e., the reaction proceeds in accord with Scheme 1, and no further investigations of the structure of the obtained products were made.

The experiments on the action of α,β-dibromodiethyl ether on phosphites were made under the usual conditions [4], i.e., on heating to 120-150° it was revealed that the reaction is exceedingly violent and leads to resinification of the reaction products. Then the experiments were run at room temperature. The course of the reaction can be followed by the change in the odor of the reactants and the change in physical constants. As easily determined constants we chose the index of refraction and specific gravity.

The experiments were run in flasks with ground-glass stoppers. The starting products – α,β-dibromodiethyl ether and the phosphites – were freshly distilled. The constants were determined immediately after the products, cooled to −10°, were poured together. The measurement results are summarized in Table 1.

The data in Table 1 show that in all of the cases studied by us the index of refraction steadily decreases with time, while the specific gravity steadily increases. At the same time there occurs almost complete disappearance of the odor, characteristic for phosphites, and the sharp odor, attacking the eyes and nose, of α,β-dibromodiethyl ether. This gives us the right to affirm that α,β-dibromodiethyl ether does add to phosphites.

TABLE 1

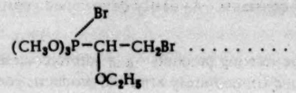
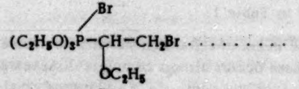
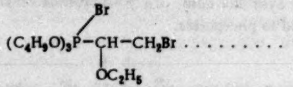
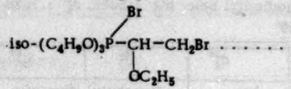
Variation in the Physical Constants for Reaction Mixtures of α,β-Dibromodiethyl Ether n_D^{20} 1.5012, d_4^{20} 1.7658 with Trialkyl Phosphites and the Constants of the Original Substances at 17-20°

Time (in days)	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}
	Trimethyl Phosphite		Triethyl Phosphite		Tributyl Phosphite		Triisobutyl Phosphite	
	1.4093	1.0493	1.4158	0.9687	1.4318	0.9133	1.4266	0.9036
	Reaction Mixture		Reaction Mixture		Reaction Mixture		Reaction Mixture	
0	1.4572	1.4050	1.4512	1.2532	1.4548	1.2068	1.4502	1.1750
1	1.4565	1.4230	1.4494	1.2646	1.4524	1.2095	1.4493	1.1786
2	1.4560	1.4447	1.4468	1.3002	1.4502	1.2103	1.4482	1.1857
3	1.4560	1.4445	1.4468	1.3025	–	–	1.4468	1.1930
4	1.4560	1.4447	1.4462	1.3042	1.4507	–	1.4462	1.1924
5	–	–	1.4462	1.3052	1.4507	1.2170	–	–
6	–	–	1.4462	1.3052	1.4509	1.2168	–	–
7	–	–	–	–	–	–	1.4462	1.1946
10	1.4560	1.4448	–	–	1.4507	1.2165	1.4462	1.1962
11	–	–	–	–	1.4506	1.2170	–	–
13	–	–	–	–	–	–	1.4462	1.1960
36	–	–	1.4460	1.3054	–	–	–	–
40	–	–	–	–	–	–	1.4462	1.1965
43	–	–	–	–	1.4507	1.2174	–	–

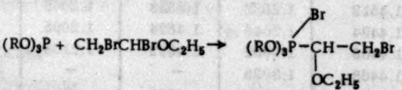
That reaction takes place is also indicated by the fact that the temperature rises on mixing the reactants. Thus, for example, on mixing trimethyl phosphite with α,β-dibromodiethyl ether, both of which had first been cooled to −3°, the temperature rose from −3° to +7°, and after vigorous shaking to 35° in 5 minutes. The heat effect is diminished with increase in the size of the phosphite radical. That a reaction takes place is also indicated by the fact that the reactant mass suffers a noticeable contraction in volume; unfortunately, we failed to make any quantitative dilatometric determinations. If the constancy of the established index of refraction and specific gravity is taken as a criterion of reaction, then it follows that the reaction at room temperature (17-20°) is completed in 3-5 days. The α,β-dibromodiethyl ether addition products are colorless, heavy, viscous liquids. Proceeding from the averages of the last determinations of the index of refraction and specific gravity we made an attempt to find the molecular refractions of the addition products and compare them with the calculated values.* The results are given in Table 2.

As follows from Table 2, the calculated and found molecular refractions fail to agree, in which connection the calculated values are always higher. Such lack of agreement can be explained by the fact that the obtained products are not chemically pure substances, or by the fact that the atomic refraction of phosphorus in these compounds is different. We attempted to obtain the addition products from α,β-dibromodiethyl ether with the phosphites in chemically pure form by crystallizing them. For this we cooled the products with liquid air, trying to obtain them in the crystalline state; however, it was revealed that the products fail to crystallize, either in the free state or in solution, but instead become hard and glassy.

TABLE 2

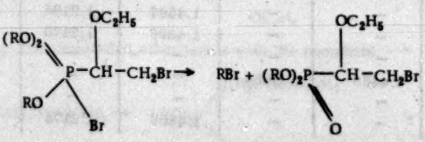
Exp. No.	Formula	n_D^{20}	d_4^{20}	MR_D	
				Calculated	Found
1	 $(CH_3O)_3P(Br)-CH(OC_2H_5)-CH_2Br$	1.4560	1.4446	64.77	66.99
2	 $(C_2H_5O)_3P(Br)-CH(OC_2H_5)-CH_2Br$	1.4462	1.3052	78.05	81.30
3	 $(C_4H_9O)_3P(Br)-CH(OC_2H_5)-CH_2Br$	1.4507	1.2170	105.76	106.54
4	 iso-$(C_4H_9O)_3P(Br)-CH(OC_2H_5)-CH_2Br$	1.4462	1.1963	105.76	107.48

All of the above clearly shows that we had obtained the addition products of α,β-dibromodiethyl ether with aliphatic esters and had realized, as a result, the first stage of the Arbuzov rearrangement:



$$(RO)_3P + CH_2BrCHBrOC_2H_5 \rightarrow (RO)_3P(Br)-CH(OC_2H_5)-CH_2Br$$

If this is so, then the products obtained by us should be capable of decomposition (in accord with the scheme proposed by Arbuzov) into alkyl bromides and the esters of α-ethoxy-β-bromoethylphosphinic acid; in other words, the second stage of this reaction can be run separately:



$$(RO)_2(RO)P(Br)-CH(OC_2H_5)-CH_2Br \rightarrow RBr + (RO)_2P(=O)-CH(OC_2H_5)-CH_2Br$$

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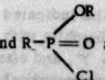
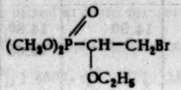
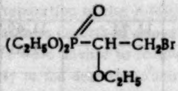
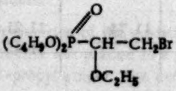
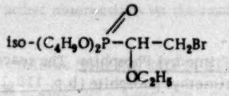
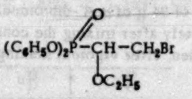
* The atomic refraction for phosphorous was taken from the compound  $R-P(OR)(Cl)=O$ and is equal to 4.270.

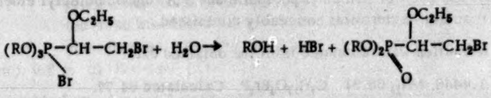
Actually, on heating to 60-140° the addition products obtained by us from α,β-dibromodiethyl ether and the aliphatic esters of phosphorous acid, the corresponding alkyl bromides are split off in yields of 80-85%, the constants of which agree well with the literature data, and the esters of α-ethoxy-β-bromoethylphosphinic acid are obtained.

That in the heating decomposition actually takes place with the cleavage of the alkyl halide, and not just simple distillation of the already cleaved alkyl halide found in the mixture, as is postulated by Kosolapoff [13], is indicated by the fact that a vacuum is formed if the addition product is placed in a flask and connected to the vacuum without heating, i.e., at room temperature. However, the vacuum is immediately destroyed if we only heat the flask to the point of incipient decomposition. The vacuum is again restored only when all of the alkyl bromide has been evolved, after which it becomes possible to distill the ester of α-ethoxy-β-bromoethylphosphinic acid. The constants of the obtained esters of α-ethoxy-β bromoethylphosphinic acid are given in Table 3.

TABLE 3
Physical Constants of the Esters of α-Ethoxy-β-bromoethylphosphinic Acid

Exp. No.	Formula	Boiling point	n_D^{20}	d_4^{20}	MR_D		Amt. of phosphorus (in %)		Yield (in %)
					Calculated	Found	Calculated	Found	
1	 $(CH_3O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	137–138° (13 mm)	1.4648	1.4402	49.68	50.08	11.87	11.51, 11.70	60.4
2	 $(C_2H_5O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	140–140.5 (9 mm)	1.4570	1.3180	58.91	59.73	10.72	10.53, 10.40	74.1
3	 $(C_4H_9O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	176–178 (12 mm)	1.4548	1.1909	77.38	78.61	8.98	9.00, 8.99	52.3
4	 $\text{iso-}(C_4H_9O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	170–171 (14 mm)	1.4523	1.1839	77.38	78.66	8.98	9.19, 8.90	53.2
5	 $(C_6H_5O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	M.p. 40–42°	–	–	–	–	8.05	8.45, 8.30	–

The addition products of α,β-dibromodiethyl ether with aliphatic phosphites, analogous to the addition product from methyl iodide and triphenyl phosphite, obtained by Michaelis and Kaehne [2], are decomposed by water:



$$(RO)_3P(Br)-CH(OC_2H_5)-CH_2Br + H_2O \rightarrow ROH + HBr + (RO)_2P(=O)-CH(OC_2H_5)-CH_2Br$$

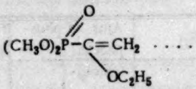
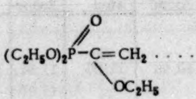
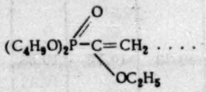
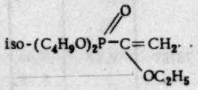
The esters of α-ethoxy-β-bromoethylphosphinic acid are isolated from the decomposition products, the constants of which are identical with the constants of the esters obtained by thermal decomposition. The second stage of the Arbuzov rearrangement was performed separately with these two reactions.

Bromomethyl n-propyl ether also reacts with triethyl phosphite with the formation of an addition product, and the reaction proceeds in two separate stages.

All of the above gives us the right to conclude that the scheme proposed by Arbuzov for explaining this reaction remains general. The first stage of the reaction, undoubtedly, proceeds by the bimolecular mechanism. In the second stage there proceeds either intramolecular decompostition of the addition product or its ionization and subsequent cleavage of the alkyl halide by the bimolecular mechanism. It seems to us that intramolecular decomposition is possible here, although for its verification a study of the structure of the addition product and the kinetics of its decomposition would be required.

From the obtained esters of α-ethoxy-β-bromoethylphosphinic acid a mole of hydrogen bromide was removed by an alcoholic potassium hydroxide solution with cooling [17]. The esters of α-ethoxyvinylphosphinic acid were obtained as a result. The constants of the obtained esters are given in Table 4.

TABLE 4
Physical Constants of Some Esters of α-Ethoxyvinylphosphinic Acid

Exp. No.	Formula	Boiling point	n_D^{20}	d_4^{20}	MR_D		Phosphorus content (in %)		Yield (in %)
					Calculated	Found	Calculated	Found	
1	 $(CH_3O)_2\overset{O}{P}-\underset{OC_2H_5}{C}=CH_2$	122–123° (10 mm)	1.4462	1.1702	41.44	41.05	17.22	17.10, 16.92	75.3
2	 $(C_2H_5O)_2\overset{O}{P}-\underset{OC_2H_5}{C}=CH_2$	128 (10 mm)	1.4408	1.0930	50.67	50.21	14.90	14.80, 14.65	76.6
3	 $(C_4H_9O)_2\overset{O}{P}-\underset{OC_2H_5}{C}=CH_2$	164–166 (13 mm)	1.4426	1.0182	69.15	68.75	11.74	11.40, 11.51	79.1
4	 iso-$(C_4H_9O)_2\overset{O}{P}-\underset{OC_2H_5}{C}=CH_2$. .	148–149 (10 mm)	1.4378	0.9954	69.15	69.44	11.74	11.21, 11.45	77.2

EXPERIMENTAL

Preparation of the Addition Product of α,β-Dibromodiethyl Ether with Trimethyl Phosphite. The reaction was carried out in a ground-glass stoppered flask, in which 18 g of freshly distilled trimethyl phosphite (b.p. 110-111°, n_D^{20} 1.4093) was placed. The flask was cooled to −3°, after which an equimolar amount of 34 g of α,β-dibromodiethyl ether (b.p. 72-74° at 15 mm, n_D^{20} 1.5012), also cooled to −3°, was added. Immediately after mixing the constants and temperature were measured, which proved to be: 7°, n_D^{20} 1.4572 and d_4^{20} 1.4050. Then, after vigorous shaking, the temperature was raised to 35° in 5 minutes, while n_D^{20} 1.4565, d_4^{20} 1.4230.

The further course of the reaction was controlled by the change in the coefficient of refraction and specific gravity. The reaction mixture was maintained at 17-19°. The observation results are given in Table 1.

After several days the odors of trimethyl phosphite and α,β-dibromodiethyl ether disappeared almost completely. The volume of the reactant mixture was noticeably diminished.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4560, d_4^{20} 1.4446, MR_D 66.91. $C_7H_{17}O_4Br_2P$. Calculated 64.77.

Preparation of the Addition Product of α,β-Dibromodiethyl Ether with Triethyl Phosphite. Triethyl phosphite, freshly distilled over sodium (b.p. 53-54° at 16 mm, n_D^{20} 1.4158), in an amount of 13 g and 18.5 g of α,β-dibromodiethyl ether, both previously cooled to −5°, were poured into the flask, which was contained in a cooling mixture. The constants were determined immediately after mixing: n_D^{20} 1.4512, d_4^{20} 1.2532.

The reaction mixture was kept cold. After 3 hours the constants were: n_D^{20} 1.4434, d_4^{20} 1.2646. Further changes in the constants are presented in Table 1, from which data it can be seen that the addition reaction is ended in 2 days.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4462, d_4^{20} 1.3052, MR_D 81.30. $C_{10}H_{23}O_4Br_2P$. Calculated 78.05.

Preparation of the Addition Product of α,β-Dibromodiethyl Ether with Triisobutyl Phosphite. The experiment was carried out the same as described above. For reaction was taken 25 g of triisobutyl phosphite (b.p. 114-116° at 13 mm), n_D^{20} 1.4266), freshly distilled over sodium, and 23.2 g of α,β-dibromodiethyl ether. The reacting components were mixed at −3°, and the constants were determined immediately: n_D^{20} 1.4502, d_4^{20} 1.1750.

Further changes in the constants are given in Table 1, from which it follows that at room temperature the reaction is ended on the sixth day.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4462, d_4^{20} 1.1963, MR_D 107.48. $C_{16}H_{35}O_4Br_2P$. Calculated 105.76.

Preparation of the Addition Product of α,β-Dibromodiethyl Ether with Tributyl Phosphite. For reaction was taken 25 g of tributyl phosphite (b.p. 124-126° at 15 mm, n_D^{20} 1.4318), freshly distilled over sodium and 23.2 g of α,β-dibromodiethyl ether. The mixing was done with cooling, and the constants of the mixture were determined immediately: n_D^{20} 1.4548, d_4^{20} 1.2068. Further changes in the constants are given in Table 1, from which it follows that at 17-19° the reaction is ended in 4 days.

The experiment was repeated several times. Heating, perceptible to the hand, was observed when the reactants were mixed at room temperature. When the reaction was run at 30-35° it was ended on the second day.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4507, d_4^{20} 1.2170, MR_D 106.54. $C_{16}H_{35}O_4Br_2P$. Calculated 105.76.

Preparation of the Addition Product of α,β-Dibromodiethyl Ether with Triphenyl Phosphite. The reaction was run the same as described above. For reaction was taken 40 g of triphenyl phosphite and 30 g of α,β-dibromodiethyl ether. We were unable to follow the course of the reaction from the coefficient of refraction. We had to limit ourselves only to the determination of odor. In this case the reaction mixture acquired an orange color. The product remained liquid.

Preparation of the Addition Product of Bromomethyl n-Propyl Ether with Triethyl Phosphite. Ten grams of triethyl phosphite was placed in a ground-glass stoppered flask, to which with cooling to −10° was added 9.2 g of bromomethyl n-propyl ether. The constants were determined immediately after mixing: n_D^{20} 1.4242, d_4^{20} 1.1425.

Further observations on the reaction course were made at room temperature. The obtained data are given in Table 5.

As follows from the data in Table 5, the reaction is ended on the second day.

n_D^{20} 1.4225, d_4^{20} 1.1447, MR_D 70.94. $C_7H_{14}O_4BrP$. Calculated 70.29.

TABLE 5

Days	n_D^{20}	d_4^{20}
1	1.4235	1.1447
2	1.4230	1.1448
3	1.4230	1.1448
15	1.4220	1.1446

Preparation of the Methyl Ester of α-Ethoxy-β-bromoethylphosphinic Acid. In an Arbuzov flask, connected to a condenser, was placed 21 g of the addition product from α,β-dibromodiethyl ether and trimethyl phosphite. The flask was heated on the water bath. When a bath temperature of 50-60° was reached the contents of the flask began to boil with the evolution of gas. The evolved gas burns, while the insertion of a copper wire in its flame imparts a green color to it. With further heating a fraction with b.p. 75-112° was collected in an amount of 1.2 g, which was not investigated. The residue was vacuum distilled. The following fractions were obtained: 1) 45-120° (13-14 mm), 3.4 g; 2) 120-130° (13-12 mm), 0.6 g; 3) 130-140° (13-12mm), 10.5 g; residue 0.6 g.

The amount of methyl bromide formed was 4.7 g (85.1%).

The 3rd fraction after repeated distillation gave 9.2 g (60%) of colorless, quite mobile liquid:

B.p. 137° (13 mm), n_D^{20} 1.4648, d_4^{20} 1.4402, MR_D 50.08. $C_6H_{14}O_4BrP$. Calculated 49.68.

0.1707 g sub.: 38.35 ml NaOH (T 0.01850; 1 ml of solution corresponds to 0.00051205 g phosphorus). 0.1684 g sub.: 38.45 ml NaOH (the same titre). Found %: P 11.51, 11.70. $C_6H_{14}O_4BrP$. Calculated %: P 11.87.

Action of Water on the Addition Product of α,β-Dibromodiethyl Ether With Trimethyl Phosphite. The addition product (15 g) of α,β-dibromodiethyl ether was treated with 50 ml of water for 1 hour. After standing, the lower layer was separated, dried over anhydrous sodium sulfate and vacuum distilled. Two successive distillations gave 5.5 g (54 %)

of the methyl ester of a -ethoxy-β -bromoethylphosphinic acid:

B.p. 137-138° (13 mm), n_D^{20} 1.4650, d_4^{20} 1.4422.

The constants are in satisfactory agreement with those for the above obtained product.

Preparation of the Ethyl Ester of a -Ethoxy-β -bromoethylphosphinic Acid. In an Arbuzov flask, fitted with condenser, was placed 30 g of the addition product from a ,β -dibromodiethyl ether and triethyl phosphite; the system was connected to the vacuum. Without heating, a vacuum of 12 mm was quickly attained, but was destroyed as soon as the bath temperature was raised to 60°. The ethyl bromide was distilled at atmospheric pressure and a bath temperature of 60-80°. The amount of distilled ethyl bromide was 7 g (85.4%).

B.p. 38-39°, n_D^{20} 1.4202, d_4^{20} 1.4302.

The residue in the flask was vacuum distilled. Two successive distillations gave 16.0 g (74.1%) of colorless, quite mobile liquid:

B.p. 142-143° (10 mm), n_D^{20} 1.4570, d_4^{20} 1.3180, MR_D 59.73. $C_8H_{18}O_4BrP$. Calculated 58.91.

0.1752 g sub.: 36.05 ml NaOH (T 0.01850). 0.1808 gssub.: 36.70 ml NaOH (T 0.01850). Found %: P 10.53, 10.40. $C_8H_{18}O_4BrP$. Calculated %: P 10.72.

Action of Water on the Addition Product From a ,β -Dibromodiethyl Ether and Triethyl Phosphite. The addition product (27 g) of a ,β -dibromodiethyl ether with triethyl phosphite was treated with 50 ml of water with shaking for 2 hours. After separating and drying the lower layer there was obatined 19.5 g of liquid, which was first distilled at atmospheric pressure. The amount of distillate at 33-44° was 1.3°. The residue was vacuum distilled. Two successive distillations gave 10.0 g (51%) of the fraction:

B.p. 142-143° (10.5 mm), n_D^{20} 1.4555, d_4^{20} 1.3148.

This is in satisfactory agreement with the data for the earlier obtained product.

The upper water layer was distilled. A fraction (4 g) with b.p. 70-90° was obtained, which gave a positive iodoform reaction.

Preparation of the n-Butyl Ester of a -Ethoxy-β -bromoethylphosphinic Acid. The addition product of a ,β -dibromodiethyl ether with tributyl phosphite was decomposed in the same manner as described above. For reaction 26 g of product was taken. At a bath temperature of 130-150° there distilled 5.8 g (81.9%) of butyl bromide:

B.p. 102-104°, n_D^{20} 1.4402, d_4^{20} 1.2742.

The residue was vacuum distilled. Two successive distillations gave 9.8 g (52.3%) of the butyl ester of a -ethoxy-β -bromoethylphosphinic acid:

B.p. 173-174° (9 mm), n_D^{20} 1.4548, d_4^{20} 1.1909, MR_D 78.61. $C_{12}H_{26}O_4BrP$. Calculated 77.38.

In a separate experiment the addition product from a ,β -dibromodiethyl ether and tributyl phosphite was decomposed in vacuo. Before the start of heating the vacuum was 20 mm; under heating the vacuum was destroyed. The butyl bromide distilled at 38° (50 mm). In the remainder the results agree.

0.2254 g sub.: 39.80 ml NaOH (T 0.01850). 0.2342 g sub.: 41.20 ml NaOH (T 0.01850). Found %: P 8.99, 9.00. $C_{12}H_{26}O_4BrP$. Calculated %: P 8.98.

Action of Water on the Addition Product from a ,β -Dibromodiethyl Ether and Tributyl Phosphite. The addition product (48 g) from a ,β -dibromodiethyl ether and tributyl phosphite was treated with 70 ml of water with shaking. After standing, the lower layer was separated and dried over anhydrous sodium sulfate. The amount of isolated substance was 36.0 g. A small amount with a wide boiling range distilled at atmospheric pressure. The residue was vacuum distilled. Two successive distillations agave the substance:

B.p. 176-178° (13.5 mm), n_D^{20} 1.4550, d_4^{20} 1.1921.

The constants agree with the earlier obtained ester.

Preparation of the Isobutyl Ester of a -Ethoxy-β -bromoethyl phosphinic Acid. In an Arbuzov flask, fitted with condenser, was placed 25 g of the addition product from a ,β -dibromodiethyl ether and triisobutyl phosphite. Boiling in the flask began at a bath temperature of 140°, while at 150-160° there distilled 5.8 g (82.3%) of isobutyl bromide:

B.p. 92-93°, n_D^{20} 1.4352, d_4^{20} 1.2632.

The residue after two successive vacuum distillations gave 9.5 g (53%) of substance:

B.p. 170-171° (14 mm), n_D^{20} 1.4523, d_4^{20} 1.1839, MR_D 78.66. $C_{12}H_{26}O_4BrP$. Calculated 77.38.

0.2026 g sub.: 36.45 ml NaOH (T 0.01850). 0.2248 g sub.: 39.00 ml NaOH (T 0.01850). Found %: P 9.19, 8.90. $C_{12}H_{26}O_4BrP$. Calculated %: P 8.98.

Action of Water on the Addition Product from α,β-Dibromodiethyl Ether and Triisobutyl Phosphite. The addition product (36 g) from α,β-dibromodiethyl ether and triisobtuyl phosphite was treated with 75 ml of water with shaking. After 1 hour the lower layer was separated, dried over sodium sulfate, and vacuum distilled. Two distillations gave 8.5 g (33 %) of the fraction:

B.p. 167-168° (11 mm), n_D^{20} 1.4520, d_4^{20} 1.1848.

Action of Water on the Addition Product from Bromomethyl n-Propyl Ether and Triethyl Phosphite. The addition product (18 g) from bromomethyl n-propyl ether and triethyl phosphite was treated with 50 ml of water with shaking. After 3 hours the lower layer was separated, dried over sodium sulfate, and vacuum distilled. The following fractions were obtained: 1) to 110° (25 to 15 mm), 2 g; 2) 110-122° (15-13 mm), 1.5 g; 3) 122-125° (10 mm), 6.2 g.

Redistillation of the 3rd fraction gave 5 g (42.4%) of the product:

B.p. 122-123° (9 mm), n_D^{20} 1.4260, d_4^{20} 1.0371, MR_D 51.88. $C_8H_{19}O_4P$. Calculated 51.15.

The constants are in satisfactory agreement with the earlier obtained ethyl ester of propoxymethylphosphinic acid [16].

Preparation of the Methyl Ester of α-Ethoxyvinylphosphinic Acid. In a flask, fitted with mechanical stirrer, reflux condenser and dropping funnel, was placed 100 ml of a 2% anhydrous alcohol solution of potassiumh hydroxide. To it with stirring and ice cooling was slowly added 9 g of the methyl ester of α-ethoxy-β-bromomethylphosphinic acid. After all of the ester had been added the reaction mixture was brought to the boil. The precipitate of potassium bromide was filtered and washed with a small portion of anhydrous alcohol. The alcohol was distilled off and the residue was vacuum distilled. Two successive distillations gave 4.7 g (75.3%) of the methyl ester of α-ethoxyvinylphosphinic acid as a colorless, quite mobile liquid with characteristic odor. Turns yellow in the air.

B.p. 122-123° (10 mm), n_D^{20} 1.4462, d_4^{20} 1.1702, MR_D 41.05. $C_6H_{13}O_4P$|F. Calculated 41.44.
0.1234 g sub.: 41.20 ml NaOH (T 0.01850). 0.1315g sub.: 40.80 ml NaOH (T 0.01850). Found %: P 17.10, 16.92. $C_6H_{13}O_4P$. Calculated %: P 17.22.

Preparation of the Ethyl Ester of α-Ethoxyvinylphosphinic Acid. The ethyl ester of α-ethoxyvinylphosphinic acid was prepared in the same manner as described above. To a solution of 5 g of potassium hydroxide in 300 ml of anhydrous alcohol with stirring and cooling was added 25.5 g of the ethyl ester of α-ethoxy-β-bromoethylphosphinic acid. After conclusion of reaction the potassium bromide was filtered, the alcohol distilled, and the residue vacuum distilled. There was obtained 14.9 g (76.6 %) of colorless liquid with characteristic odor:

B.p. 128-130° (10 mm), n_D^{20} 1.4408, d_4^{20} 1.0930. MR_D 50.21. $C_8H_{17}O_4P$ |F. Calculated 50.67.

0.1958 g sub.: 56.50 ml NaOH (T 0.01850). 0.1734 g sub.: 49.90 ml NaOH (T 0.01850). Found %: P 14.80, 14.65. $C_8H_{17}O_4P$. Calculated %: P 14.90.

Preparation of the n-Butyl Ester of α-Ethoxyvinylphosphinic Acid. To a solution of 3 g of potassium hydroxide in 150 ml of anhydrous alcohol with stirring and cooling was added 18 g of the n-butyl eser of α-ethoxy-β-bromoethylphosphinic acid. After filtering off the potassium bromide and distilling off the alcohol the residue was vacuum-distilled. There was obtained 10.8 g (79.1 %) of the n-butyl ester of α-ethoxyvinylphosphinic acid as a liquid with characteristic odor, turning yellow in the air:

B.p. 164-166° (13 mm), n_D^{20} 1.4426, d_4^{20} 1.0182. MR_D 68.75. $C_{12}H_{25}O_4P$|F. Calculated 69.15.
0.2186 g sub.: 48.65 ml NaOH (T 0.01850). 0.2040 g sub.: 45.80 ml NaOH (T 0.01850). Found %: P 11.40, 11.51. $C_{12}H_{25}O_4P$. Calculated %: P 11.74.

Preparation of the Isobutyl Ester of α-Ethoxyvinylphosphinic Acid. To a solution of 2.6 g of potassium hydroxide in 150 ml of anhydrous alcohol with stirring and cooling was added 13 g of the isobutyl ester of α-ethoxy-β-bromoethylphosphinic acid. After removal of the ptoassium bromide and distilling off the alcohol the residue was vacuum-distilled. There was obtained 7.5 g (77.2 %) of the isobutyl ester of α-ethoxyvinylphosphinic acid:

B.p. 148-149° (10 mm), n_D^{20} 1.4378, d_4^{20} 0.9954, MR_D 69.44. $C_{12}H_{25}O_4P$. Calculated 69.15.

0.1918 g sub.: 42.85 ml NaOH (T 0.01850). Found %: P 11.45. $C_{12}H_{25}O_4P$. Calculated %: P 11.74.

SUMMARY

1. It was shown that the reaction of α-β-dibromodiethyl ether with esters of phosphorous acid gives addition products.

2. It was shown that heating of the addition products obtained from α,β-dibromodiethyl ether and phosphites results in the cleavage of alkyl halide and the esters of α-ethoxy-β-bromoethylphosphinic acid are formed. The same esters are obtained by the action of water on the addition products.

3. As a result, it was shown that the Arbuzov reaction for the rearrangement of phosphites, obtained from aliphatic alcohols, can be run in two separate independent stages. In this way it was shown that the scheme proposed by A. E. Arbuzov remains the general scheme for this reaction.

4. It was shown that the cleavage of hydrogen bromide from the esters of α-ethoxy-β-bromoethylphosphinic acid results in the formation of the esters of α-ethoxyvinylphosphinic acid.

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OXIDATION OF ESTERS OF 9-OCTADECENOIC ACIDS

✓ N. P. Bulatsky

We had communicated earlier [1] that the geometric isomers of 9-octadecenoic acid are oxidized at a different rate by potassium permanganate in acetone solution.

At the suggestion of A. K. Plisov this observation was transferred to the oxidation of the methyl, ethyl, propyl and butyl esters of oleic and elaidic acids for the purpose of elucidating the influence of the alcohol radical structure and the dependence of reactivity on the spatial configuration of the molecule.

The performed studies revealed that the oxidation rate depends on both the spatial configuration of the molecule and the structure of the alcohol radicals entering into the composition of the ester.

EXPERIMENTAL

The esters of oleic and elaidic acids were obtained by the esterification of the acids with the anhydrous alcohol in the presence of sulfuric acid [2]. The properties of the obtained esters are given in Table 1.

TABLE 1

Ester	Boiling point at the pressure (in mm)		Saponification Number	Iodine Number (by Hubel)
Methyl oleate	178°	(5)	190	85.93
Ethyl oleate	182	(5)	180.3	81.29
Propyl oleate	184.5	(5)	171.9	78.39
Butyl oleate	194	(5)	166.0	73.88
Methyl elaidate	178.4	(5)	188.6	84.96
Ethyl elaidate	183	(5)	181.2	82.30
Propyl elaidate	186	(5)	172.4	77.64
Butyl elaidate	196	(5)	166.2	73.62

TABLE 2

Experimental Temperature 20°; Concentration of Oxidized Esters 0.0442 N.; Concentration of Oxidizing Agent 0.0410 N.

Time of oxidation (min.)	Amount of Thiosulfate (in ml)							
	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate	Methyl elaidate	Ethyl elaidate	Propyl elaidate	Butyl elaidate
15	6.64	6.72	6.81	7.00	7.42	7.54	7.63	7.61
30	5.38	5.48	5.72	5.81	6.73	6.78	6.82	6.91
45	4.49	4.58	4.69	4.97	5.96	6.03	6.06	6.12
60	3.74	3.83	3.85	4.09	5.28	5.26	5.53	5.58
75	2.92	3.20	3.30	3.37	4.60	4.66	4.60	4.68
90	2.35	2.49	2.52	2.68	3.68	3.78	3.92	3.98

The oxidation studies were made in the same way as is described in detail in the experiments with the free acids [1].

The results of the experiments, run at different temperatures and different concentrations of esters and oxidizing agent, are given in Tables 2-4.

TABLE 3

Experimental Temperature 10°; Concentration of Oxidized Esters 0.0442 N.; Concentration of Oxidizing Agent 0.0410 N.

Time of oxidation (min.)	Amount of Thiosulfate (in ml)							
	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate	Methyl elaidate	Ethyl elaidate	Propyl elaidate	Butyl elaidate
30	6.86	6.82	6.99	7.14	7.55	7.61	7.78	7.83
60	5.56	5.65	5.97	5.93	6.84	7.02	7.10	7.12
90	4.63	4.78	4.96	5.11	6.16	6.39	6.55	6.56
120	3.95	3.97	4.10	4.27	5.60	5.75	5.90	5.98
150	3.14	3.35	3.51	3.57	4.96	5.20	5.30	5.42
180	2.32	2.53	2.78	2.82	4.22	4.60	4.67	4.78

TABLE 4

Experimental Temperature 20°; Concentration of Oxidized Esters 0.0221 N.; Concentration of Oxidizing Agent 0.0451 N.

Time of oxidation (min.)	Amount of Thiosulfate (in ml)							
	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate	Methyl elaidate	Ethyl elaidate	Propyl elaidate	Butyl elaidate
15	8.84	8.76	8.92	8.95	9.35	9.30	9.42	9.50
30	7.95	8.08	8.20	8.18	8.60	8.74	8.80	8.78
45	7.39	7.47	7.50	7.52	8.08	8.02	8.16	8.15
60	6.75	6.80	6.94	7.10	7.54	7.41	7.49	7.62
75	6.49	6.56	6.52	6.68	6.94	7.08	7.12	7.12
90	5.99	6.04	6.14	6.18	6.54	6.68	6.68	6.70

The obtained data (Tables 2-4) indicate that the esters of oleic (cis-) acid are more rapidly oxidized with potassium permanganate in acetone solution than are the corresponding esters of elaidic (trans-) acid.

From the data in Tables 2-4 it can be seen that in measure with increase in the alcohol radical (from methyl to butyl) that the oxidation rate of the esters of both oleic and elaidic acids is diminished.

SUMMARY

1. The esters of oleic acid are more rapidly oxidized with potassium permanganate in acetone solution than are the esters of elaidic acid.

2. An increase in the size of the alcohol radical in the ester molecule leads to a redutcion in the oxidation rate.

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Odessa State University

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* Consultants Bureau Translation, p. 1845.

OXIDATION OF VINYLACETYLENE HYDROCARBONS WITH ORGANIC HYDROPEROXIDES

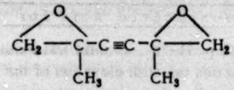
III. OXIDATION OF 3,6 DIMETHYL-2,6-OCTADIEN-4-YNE WITH ACETYL HYDROPEROXIDE (PEROXYACETIC ACID)

N. M. Malenok and S. D. Kulkina

In previous papers [1] we communicated the results obtained by us on the oxidation of vinylacetylene hydrocarbons of diverse structure with acetyl hydroperoxide (peroxyacetic acid).

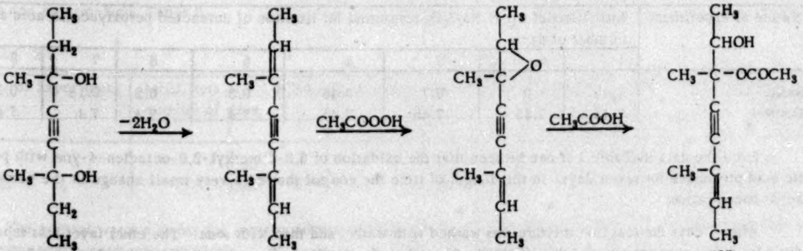
In the present paper we oxidized the divinylacetylene hydrocarbons with peroxyacetic acid for the purpose of obtaining their first product – the acetylene diepoxide and studying its properties.

The reason for this was the fact that the acetylene diepoxides have been studied but slightly. In this field are known the investigations of Gershtein [2], who in the reaction of the acetylene dichlorohydrin dichlorotetramethylbutynediol with powdered KOH obtained two stereoisomers of the acetylene diepoxide:



(I)

The hydrolysis of these diepoxides gave acetylene erythritols, in which the presence of hydroxyl groups was demonstrated by preparing the tetraacetyl derivatives. For obtaining the divinylacetylene hydrocarbon – 3,6-dimethyl-2,6-octadien-4-yne (III) – we first synthesized from methyl ethyl ketone and acetylene glycol by the method of Zh. I. Iotsich the compound 3,6-dimethyl-4-octyn-3,6-diol (II), which was dehydrated with 40% H_2SO_4 to the unsaturated hydrocarbon (III). Its oxidation with one mole of peroxyacetic acid gave the vinylacetylene alcohol acetate – 3,6-dimethyl-3-acetoxy-6-octen-4-yn-2-ol (V), which proves to be a secondary product, formed from the vinylacetylene monoepoxide (IV) and acetic acid; in this connection the acetylene diepoxide – 3,6-dimethyl-2,3,6-7-diepoxy-4-octyne (VI) was also isolated.

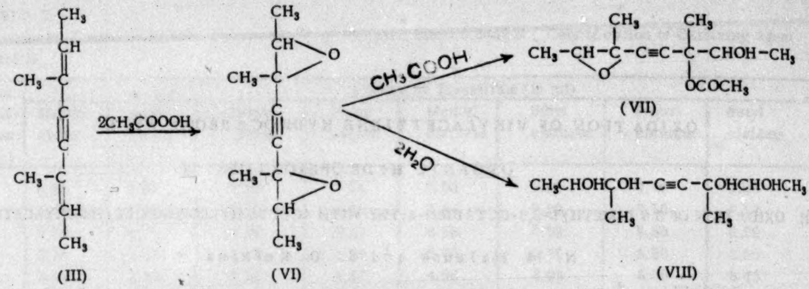


(II) (III) (IV) (V)

The oxidation of 3,6-dimethyl-2,6-octadien-4-yne with two moles of peroxyacetic acid gave the same acetylene diepoxide that was obtained in the first case (VI) and also the monoepoxide – 3,6-dimethyl-6-acetoxy-2,3-epoxy-4-octyn-7-ol (VII), which was formed by the reaction of the diepoxide with acetic acid.

The diepoxide was subjected to hydrolysis; the result was the acetylene erythritol – 3,6-dimethyl-4-octyn-2,3,6,7-tetrol (VIII).

The oxidation of the hydrocarbon (III) with 4 moles of peroxyacetic acid, calculated on the basis of oxidizing two double bonds and one triple bond, gave the same monoepoxide (VII) as was obtained in the previous case.



The presence of a triple bond in this substance and in the erythritol was demonstrated by quantitative bromination. As a result, in the oxidation of divinylacetylene hydrocarbons with peroxyacetic acid the oxidation proceeds at the double bonds, while the triple bond remains untouched.

We observed a similar phenomenon also in the oxidation of vinylacetylene hydrocarbons with peroxyacetic acid in which the hydrogens at the carbon atoms of the triple bond were susbtituted by hydrocarbon radicals [3].

EXPERIMENTAL

Oxidation of 3,6-Dimethyl-2,6-octadien-4-yne with Peroxyacetic Acid Calculated on the Basis of 2 Moles of Peroxyacetic Acid for 1 Mole of Hydrocarbon

The divinylacetylene hydrocarbon (57.5 g) (b.p. 71-73°, 20 mm) was oxidized in anhydrous diethyl ether with 173 g of 38% peroxyacetic acid at −8°. The reaction ran with elevation of the temperature to −5°. After all of the peroxyacetic acid had been added to the hydrocarbon the reaction mixture was let stand at room temperature.

Together with the oxidation of the divinylacetylene hydrocarbon by peroxyacetic acid a control was run under similar conditions.

The oxidation progress for both the basic and control experiments was determined daily by titration with 0.1 N $Na_2S_2O_3$ solution. For this 20 ml aliquots of the experimental and control solutions that had been previously diluted 100-fold with water were taken and the amount of unreacted peroxyacetic acid determined iodometrically. The results are given in Table 1.

TABLE 1

Nature of Experiment	Milliliters of 0.1 N $Na_2S_2O_3$ consumed for titration of unreacted peroxiyacetic acid after number of days:							
	1	2	3	4	5	6	7	8
Basic	7.45	1.0	0.7	0.45	0.3	0.2	0.15	0.15
Control	7.45	7.45	7.45	7.45	7.4	7.4	7.4	7.4

From the data in Table 1 it can be seen that the oxidation of 3,6-dimethyl-2,6-octadien-4-yne with peroxyacetic acid proceeded for seven days. In this length of time the control showed a very small change in the peroxyacetic acid concentration.

After 7 days the reaction mixture was washed with water, and then with soda. The ether layer was separated, dried for a day over potash, and then filtered. The ether was distilled off, and from the residual mass a 3-fold fractional distillation gave two substances: 1) b.p. 62-64° (0.5 mm), 4.2 g; 2) b.p. 121-122° (1 mm), 16.4 g.

Investigation of the Substance with B.P. 62-64° (0.5 mm). Lachrymatory liquid with a light yellow color. Soluble in diethyl ether, ethyl alcohol and chloroform, insoluble in water.

d_{20}^{20} 0.9630, n_D^{20} 1.4587, MR_D 47.09; calculated 46.66.

0.1294 g sub.: 0.3483 g CO_2; 0.1001 g H_2O. 0.1055 g sub.: 0.2833 g CO_2; 0.0820 g H_2O. 0.2303 g sub.: 23.03 g benzene: Δt 0.332°. Found %: C 73.41, 73.24; H 8.65, 8.69. M 155.6. $C_{10}H_{14}O_2$. Calculated %: C 72.29; H 8.43. M 166.

In acid medium the obtained diepoxide – 3,6-dimethyl-2,3,6,7-diepoxy-4-octyne (VI) – liberates iodine from potassium iodide and fails to show the presence of active hydrogen with methylmagnesium iodide.

The high content of carbon in the diepoxide when compared to theory is, apparently, due to some impurity, which is removed only with difficulty.

Investigation of the Substance with B.P. 121-122° (1 mm). The viscous liquid is soluble in the same solvents as the diepoxide; in soluble in water.

d_{20}^{20} 1.0585, n_D^{20} 1.4671, MR_D 59.01; calculated 58.94.

0.1259 g sub.: 0.2956 g CO_2; 0.0957 g H_2O. 0.1287 g sub.: 0.2998 g CO_2; 0.0958 g H_2O. 0.2588 g sub.: 22.9 g benzene; Δt 0.251°. 0.2624 g sub.: 27.9 ml CH_4 (15°, 744 mm). Found %: C 64.02, 63.53; H 8.42, 8.27; OH 7.54, M 230.9. $C_{12}H_{18}O_4$. Calculated %: C 63.72; H 7.98; OH 7.52. M 226.

Hydrolysis of the Diepoxide – 3,6-Dimethyl-2,3,6,7-diepoxy-4-octyne. Two grams of the diepoxide was heated on the water bath to 60° with 15 ml of water in the presence of HCl traces for 2 hours. The result was a solution with a small amount of tarry residue. After removing the tar the liquid was evaporated on the water bath. A crystalline substance was obtained, insoluble in ether, benzene and chloroform, and readily soluble in ethyl alcohol and water. After repeated washing with diethyl ether there was obtained 1.4 g of crystals with m.p. 134-136°.

0.1194 g sub.: 0.2589 CO_2; 0.0943 g H_2O. 0.1126 g. sub.: 0.2449 g CO_2; 0.0946 g H_2O. 0.2015 g sub.: 16.58 g H_2O; Δt 0.114°. Found %: C 59.14, 59.32; H 8.84, 9.38. M 198.5. $C_{10}H_{18}O_4$. Calculated %: C 59.41; H 8.98. M 202.

The analysis data show that the crystalline substance is the acetylene erythritol – 3,6-dimethyl-4-octyn-2,3,6,7-tetrol.

We were unable to determine the number of hydroxyl groups in it due to its insolubility in isoamyl ether and anisole.

The presence of a triple bond in the acetylene erythritol was shown by quantitative bromination.

0.2010 g of substance, dissolved in water, added 0.3345 g of bromine, which corresponds to theory for the addition of 4 atoms of bromine or 0.3184 g for 1 triple bond.

Oxidation of 3,6-Dimethyl-2,6-octadien-4-yne with Peroxyacetic Acid Calculated on the Basis of 1 Mole of Peroxyacetic Acid for 1 Mole of Hydrocarbon

The divinylacetylene hydrocarbon (33 g) was oxidized in anhydrous diethyl ether with 50 g of 38% peroxyacetic acid at –5°. The reaction proceeded with elevation of the temperature to 0° and was completed on the third day, which can be seen from Table 2.

TABLE 2

Nature of Experiment	Milliliters of 0.1 N $Na_2S_2O_3$ consumed for titration of unreacted peroxyacetic acid after number of days:			
	1	2	3	4
Basic	5.65	0.25	0.05	0.05
Control	5.65	5.65	5.65	5.65

The control was run under the same conditions as the experiment and for four days failed to show a change in the peroxyacetic acid concentration.

The diethyl ether, formed acetic acid and unreacted peroxyacetic acid were separated from the oxidation products the same as in the previous case. From the residual mass a 3-fold fractional distillation gave two substances: 1) b.p. 62-64° (0.5 mm), 2.5 g, which proved to be the diepoxide – 3,6-dimethyl-2,3,6,7-diepoxy-4-octyne (VI), and 2) b.p. 95-96° (0.5 mm), 6 g.

Investigation of the Substance with B.P. 95-96° (0.5 mm). Soluble in diethyl ether, chloroform and acetone, insoluble in water.

d_{20}^{20} 0.9936, n_D^{20} 1.4779, MR_D 59.81; calculated 58.33.

0.1304 g sub.: 0.3295 g CO_2; 0.1030 g H_2O. 0.1141 g sub.: 0.2863 g CO_2; 0.0930 g H_2O. 0.1994 g sub.: 23.99 g benzene: Δt 0.206°; 0.1226 g sub.: 15.85 ml CH_4 (15°, 751 mm). Found %: C 68.91, 68.43; H 8.77, 9.06; OH 9.53. M 207.4. $C_{12}H_{18}O_3$. Calculated %: C 68.57; H 8.57; OH 8.10. M 210.

The investigated substance is the vinylacetylene alcohol acetate – 3,6-dimethyl-3-acetoxy-6-octen-4-yn-2-ol (V).

Oxidation of 3,6-Dimethyl-2,6-octadien-4-yne with Peroxyacetic Acid Calculated on the Basis of 4 Moles of Peroxyacetic Acid for 1 Mole of Hydrocarbon

The divinylacetylene hydrocarbon (21 g) was oxidized with 160 g of peroxyacetic acid under the same conditions as in the previous cases. The result was the isolation of only one substance with b.p. 121-122° (1mm) in amount of 7.6 g, which on investigation proved to be the monoepoxide – 3,6-dimethyl-6-acetoxy-2,3-epoxy-4-octyn-7-ol (VII), obtained by us earlier.

The presence of a triple bond in this substance was determined by quantitative bromination.

0.3785 g of substance, dissolved in chloroform, added 0.4676 g of bromine. The calculated theory should have resulted in the addition of 0.5360 g of bromine for 1 triple bond.

The low amount of bromine added to the substance, when compared to theory, can be explained by slight evaporation of the solvent – chloroform – under prolonged bromination (6 hours).

SUMMARY

1. The oxidation of 3,6-dimethyl-2,6-octadien-4-yne with one mole of peroxyacetic acid gave the vinylacetylene alcohol acetate – 3,6-dimethyl-3-acetoxy-6-octen-4-yn-2-ol and the diepoxide, the hydrolysis of which gave the acetylene erythritol – 3,6-dimethyl-4-octyn-2,3,6,7-tetrol.

2. The oxidation of 3,6-dimethyl-2,6-octadien-4-yne with two moles of peroxyacetic acid gave the acetylene diepoxide and the monoepoxide – 3,6-dimethyl-6-acetoxy-2,3-epoxy-4-octyn-7-ol, which is also formed when the hydrocarbon is oxidized with 4 moles of peroxyacetic acid.

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[2] N. A. Gershtein, J. Gen. Chem. 9, 361 (1939).

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Minsk Institute of Medicine

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* Consultants Bureau Translation, p. 1181.

** Consultants Bureau Translation, p. a-151.

UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XVI. ACTION OF METALLIC SODIUM ON 2,3-DIBROMO-1,3-CYCLOHEXADIENE

N. A. Domnin, G. K. Krasilnikova and V. A. Cherkasova

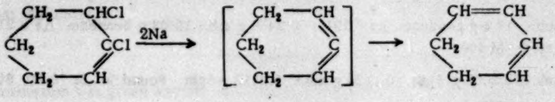
It had already been shown earlier by one of us [1] that in the action of metallic sodium or zinc dust on 1,2-dichloro-2-cyclohexene (I) the expected isomer of the originating 1,2-cyclohexadiene, namely 1,3-cyclohexadiene, is not formed at all; here it was shown by us that the reaction proceeds only by way of polymerization, the mechanism of which remains obscure.

The problem remained unsolved as to the main reason for making it impossible for the isomerization reaction to proceed in the direction of forming the monomeric products.

As a result of reaction with metallic sodium the polymeric products are completely devoid of chlorine, which means that the 1,2-dichloro-2-cyclohexene (I) completely releases all of its chlorine to the metallic sodium.

It was shown by D. V. Tishchenko [2] that the formation of 1,2-cyclohexadiene (II) as an intermediate reaction product takes place in the action of quinoline on 1,2,2-trichlorocyclohexane, as a result of which 1-chloro-1,3-cyclohexadiene is formed.

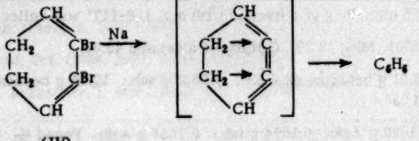
If for our case it is assumed that as intermediate product the short-lived 1,2-cyclohexadiene (II) is formed, then according to generally established opinion [3] it should easily suffer isomerization through the shifting of one hydrogen atom in the beta-position to 1,3-cyclohexadiene (III).



(I) (II) (III)

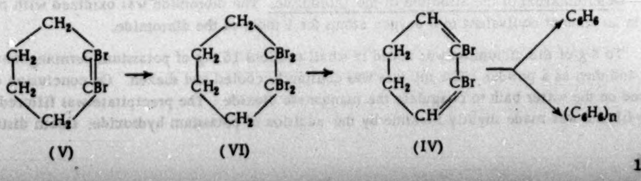
Since the reaction completely fails to proceed in this reaction, then it must be assumed that hydrogen shifting fails to occur here.

The question relative to the difficulty or ease of hydrogen shifting in general up to now remains slightly developed with respect to unsaturated cyclic and bicyclic hydrocarbons; consequently, it appeared ot interest to us to attempt the introduction of even some clarity into the picture. For the realization of this attempt we started from the compound, which, in the creation of cumulative double bonds in its molecule, could easily be isomerized into the stable monomeric form – the benzene ring



(IV)

It was proposed to conduct the investigation in accord with the following scheme:



(V) (VI) (IV)

The structure of the starting 1,2-dibromo-1-cyclohexene (V) was shown by Favorsky and Bozhovsky [4]; the structure of the 1,1,2,2-tetrabromocyclohexane (VI) was shown by us via the fact that in the action of zinc dust on it two bromine atoms are split off and the starting 1,2-dibromo-1-cyclohexene (V) is obtained.

The structure of the 2,3-dibromo-1,3-cyclohexadiene (IV) was demonstrated by its oxidation with potassium permanganate to succinic and oxalic acids.

As a result of the performed work it was shown that in the action of zinc dust on 2,3-dibromo-1,3-cyclohexadiene (IV) the compound fails to release its bromine atoms to the zinc; metallic sodium removes both of the bromine atoms from 2,3-dibromo-1,3-cyclohexadiene (IV) but as a result of this reaction only a polymeric product is formed.

EXPERIMENTAL

1,2-Dibromo-1-cyclohexene was synthesized by the earlier described method [4].

Preparation of 1,1,2,2-Tetrabromocyclohexane. To 20 g of 1,2-dibromo-1-cyclohexene in chloroform (1:1) was added with cooling 4.2 ml (13.4 g) of bromine in chloroform (1:1), and the mixture was allowed to stand for a day at room temperature. Then the mixture was heated for an hour at 30-40° and to the heated mixture was added 1-1.5 ml of distilled water. Slight evolution of hydrogen bromine was observed, but the mixture failed to decolorize; for that reason it was let stand for another day at room temperature, and then it was again heated to 30-40°. The unreacted bromine was removed by washing with dilute sodium sulfite solution, and the treated solution was washed with water and dried over calcium chloride. The solvent was removed with an oil pump into a trap, immersed in a cooling mixture of dry ice and ether. The residue was distilled at 10 mm. The fraction collected in the range 100-112° crystallized completely and proved to be the starting 1,2,-dibromo-1-cyclohexene. With further elevation of the temperature the residue in the flask began to decompose. With ordinary cooling of the flask the residue crystallized completely. The crystalline mass was extracted with ether from the flask, poured into a crystallizing dish and after removal of the ether it again crystallized. The crystals, pressed on porous plate, melted at 188 190°, with slight decomposition and on standing partially evolved hydrogen bromide and bromine.

After recrystallization from ethyl alcohol stable colorless crystals with m.p. 209° were obtained. From 20 g of the dibromide there was obtained 8.2 g of pure crystalline 1,1,2,2-tetrabromocyclohexane.

0.2629 g sub.: 17.4 g benzene: Δt 0.191°. 0.2456 g sub.; 15.03 g benzene: Δt 0.21°. Found: M 394.3, 396. $C_6H_8Br_4$. Calculated: M 400.

0.1388 g sub.:. 0.2608 g AgBr. 0.1124 g sub.: 0.2119 g AgBr. Found %: Br 79.90, 80.24. $C_6H_8Br_4$. Calculated %: Br 79.90.

To determine its structure the 1,1,2,2-tetrabromocyclohexane was treated with zinc dust in boiling dioxane. In this way an almost quantitative yield of the starting 1,2-dibromo-1-cyclohexene was obtained, the mixed melting point of which with authentic 1,2-dibromo-1-cyclohexene was 39-40° and failed to show a depression.

Cleavage of Hydrogen Bromide from 1,1,2,2-Tetrabromocyclohexane. The crystalline tetrabromide was added to a boiling 20% alcohol solution of potassium hydroxide, which was taken in excess (30%). The mixture was heated on the water bath for 4 hours, and after cooling was diluted with water to complete solution of the precipitated potassium bromide. The formed dibromide separated as an oil on the bottom of the flask. The oil was separated, dissolved in ether, the solution washed several times with water, and dried over calcium chloride. After distilling off the ether the residue was distilled at 25 mm; 20 g of a fraction with b.p. 116-117° was collected.

d_4^{20} 1.8490, n_D^{20} 1.5701, MR_D 42.23. $C_6H_6Br_2$. Calculated 42.00.

0.2973 g sub.: 12.51 g benzene: Δt 0.52°. 0.2343 g sub.: 12.25 g benzene: Δt 0.36°. Found M 235, 234. C_6H_6Br. Calculated: M 238.

0.1196 g sub.: 0.1882 g AgBr. 0.1074 g sub.: 0.1687 g AgBr. Found %: Br 66.91, 66.86. C_6H_6Br. Calculated %: Br 67.92.

Determination of the Structure of the Dibromide. The dibromide was oxidized with potassium permanganate, taken in an amount equivalent to 6 oxygen atoms for 1 mole of the dibromide.

To 6 g of the dibromide was added in small portions 15.8 g of potassium permanganate, first as a saturated solution and then as a powder. The mixture was constantly cooled and shaken. On conclusion of oxidation the mixture was heated on the water bath to coagulate the manganese dioxide. The precipitate was filtered and washed with hot water. The filtrate was made slightly alkaline by the addition of potassium hydroxide; steam distillation failed to disclose any neutral products. The filtrate was evaporated, acidified with sulfuric acid, and extracted with diethyl ether for 2 days.

The yield of crystalline acid was 1.2 g, which after recrystallization from water and drying melted at 182.5-183°. The mixed melting point of this acid with authentic succinic acid failed to be depressed.

0.1140 g sub.: 19.2 ml 0.1 N NaOH. 0.1215 g sub.: 20.5 ml 0.1 N NaOH. Found equiv. 59.20, 59.11. $C_4H_6O_4$. Calculated: equiv. 59.00.

0.1567 g salts: 0.1008 g Ag. Found %: Ag 64.43. $C_4H_4O_4Ag_2$. Calculated %: Ag 65.03.

The dibromide fails to condense with maleic anhydride.

Cleavage of Bromine from 2,3-Dibromo-1,3-cyclohexadiene. In a thick-walled tube was placed 7 g of freshly-cut metallic sodium in 20 ml of anhydrous dioxane. The end of the tube was tightly closed with a stopper with calcium chloride tube. After complete cessation of hydrogen bubble evolution there was introduced into the tube 10 g of 2,3-dibromo-1,3-cyclohexadiene; after this the tube was sealed and let stand at room temperature until reaction was complete.

The reaction of metallic sodium with the dibromide began immediately. The sodium pieces began to blacken on the corners and edges, and then the whole mixture turned dark. After two days the tube was opened, the solution decanted from the sodium bromide precipitate and remaining metallic sodium, while the residue was washed several times with dioxane. The solution was filtered to remove turbidity and then diluted with water; here a weakly stable emulsion was formed and on the walls of the separatory funnel there deposited yellow flocs of polymerization products. We failed to disclose the presence of even traces of any monomers or the expected benzene. In the reaction tube in measure with dioxane removal there also separated a light yellow mass of polymerization products. They were extracted with ether, boiled with distilled water, and then dried. About 2 g of the pure polymers was obtained. The hard amorphous substance is readily soluble in ether, benzene and dioxane. The qualitative test for halogen was negative.

0.1347 g sub.: 16.56 g benzene: Δt 0.14°. 0.2215 g sub.: 11.03 g benzene: Δt 0.33°. Found M 297, 312. $(C_6H_4)_4$. Calculated: M 320.

The elementary analysis of the polymer for carbon and hydrogen failed to give consistent results, since the polymer burns only with great difficulty.

SUMMARY

1. A full characterization was given and the structure of 2,3-dibromo-1,3-cyclohexadiene was proven.

2. It was shown that the action of metallic sodium on 2,3-dibromo-1,3-cyclohexadiene completely fails to give any of the theoretically possible benzene, but instead only polymerization products are formed.

3. The present work raised some new questions on the mechanism of polymerization, on the ease or difficulty of shifting hydrogen atoms in different cases, on the stability of different types of deformed molecules, on the impossibility of their temporary origin, etc.

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Leningrad State University

[illegible]. The filtrate was [illegible], acidified with [illegible] acid, and extracted with [illegible]

The yield of crystalline acid was 2.4 g [illegible]

The mixed melting point of this acid with [illegible] acid [illegible] to be depressed.

0.1140 g sub.: 13.2 ml 0.1 N NaOH. 0.1210 g sub.: [illegible] ml 0.1 N NaOH. [illegible]

Calculated: [illegible]

[illegible] g sub.: [illegible] g [illegible]. Found: [illegible]

The [illegible] with [illegible].

Cleavage of [illegible] from 2,3-[illegible]. In a thick-walled tube was placed [illegible] in 20 ml of [illegible]. The end of the tube was [illegible] [illegible] [illegible]

The [illegible] of [illegible] [illegible]. [illegible]

0.1 [illegible] g sub.: 15.50 g benzene: [illegible]

Calculated: M [illegible].

The elementary analysis of the [illegible] [illegible] with great difficulty.

SUMMARY

1. A [illegible] was given and the [illegible]

2. It was shown that the [illegible]

3. The [illegible] in different cases, on the [illegible] the [illegible] temporary [illegible], etc.

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(2) B. V. Tishchenko, J. Gen. Chem. 8, [illegible]

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Leningrad State University

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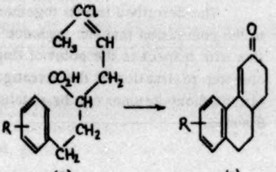
SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

VIII. 8-METHYL- AND 8-METHOXY-3-KETO-1,2,3,9,10,10a-HEXAHYDROPHENANTHRENES

G. T. Tatevosyan and A. G. Vardanyan

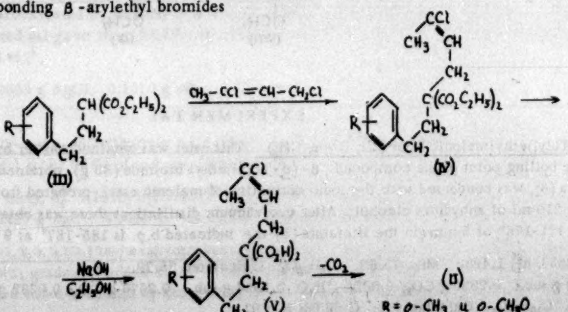
In previous communications it was shown that the yields of substituted 3-keto-1,2,3,9,10,10a-hexahydrophenanthrenes (I), formed in the reaction of α-(3-chlorocrotyl)-γ-phenylbutyric acids (II) with sulfuric acid, are influenced by the presence of methyl and methoxy groups in the meta- and para-positions of the aromatic ring


(II) (I)

It was found that the methyl group, irrespective of whether it is found in the meta- or para-position with respect to the side chain (II, R = m- or p-CH_3), fails to exert any marked influence on the yield of the corresponding tricyclic ketone [1], while at the same time the position of the methoxyl group strongly influences the course of the studied conversion [2]. Whereas the methoxyl group found in the meta-position (II, R = m-CH_3O), not changing the basic course of the reaction, only slightly lowers the yield of tricyclic ketone (I, R = 7-CH_3O), which, apparently, is explained by the comparative ease with which the methoxylated aromatic ring is sulfonated, the same group in the para-position (II, R = p-CH_3O) completely excludes the possibility of a one-step realization of this transformation; the starting acid, similar to the γ-phenylbutyric acid not substituted in the side chain [3], when treated with sulfuric acid is practically completely sulfonated. This result can be explained as being due to the ease with which the methoxylated ring sulfonates and also to the circumstance that the methoxyl group, being strongly ortho-, para-orienting, prevents the intramolecular acylation that should take place at the meta-position with respect to this group.

For the purpose of obaining the complete picture on the influence of alkyl (for example methyl) and alkoxyl (for example methoxyl) groups on the yields of 3-keto-hexahydrophenanthrenes obtained by the indicated method a study was made of the analogous conversion of α-(3-chlorocrotyl)-γ-phenylbutyric acids in which the same substituents were contained in the ortho-position of the aromatic ring (II, R = o-CH_3 and o-CH_3O).

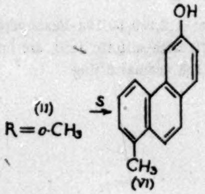
The starting acids (II, R = o-CH_3 and o-CH_3O) were obtained via the malonic ester synthesis from 1,3-dichloro-2-butene and the corresponding β-arylethyl bromides


(III) (IV) (V) (II)

The reaction of α-(3-chlorocrotyl)-γ-(o-tolyl)butyric acid (II, R = o-CH_3) with sulfuric acid (d 1.78) at 60-75° gave 3-keto-8-methyl-1,2,3,9,10,10a-hexahydrophenanthrene (I, R = 8-CH_3). The yield of this ketone (62.95%) was of the same order as the yields of the unsubstituted ketone and its two other methyl homologs [1].

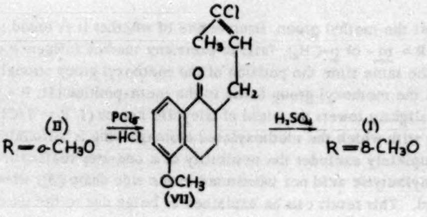
The dehydrogenation of the ketone with sulfur gave 3-hydroxy-8-methylphenanthrene (VI).

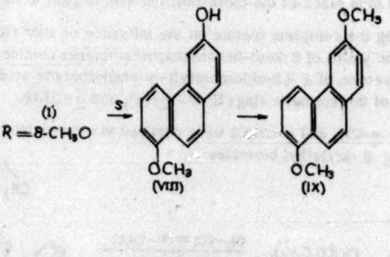
α-(3-Chlorocrotyl)-γ-(o-anisyl)butyric acid (II, R = o-CH_3O), similar to its p-anisyl isomer, is completely sulfonated under the influence of sulfuric acid. In this case also the tricyclic methoxy ketone (I, R = 8-CH_3O) can be obtained only in a circuitous manner, consisting in the thermal dehydrochlorination of the acid chloride of the acid (II, R = o-CH_3O), subsequent hydrolysis, and intramolecular aldol condensation of the substituted tetralone (VII) under mild conditions, not favorable to sulfonation.



The structure of the methoxy ketone (I, R = 8-CH_3O), evolving from its method of preparation, was confirmed by its dehydrogenation to 3-hydroxy-8-methoxyphenanthrene (VIII) and methylation of the latter to 3,8-dimethoxyphenanthrene (IX), described earlier in the literature [4].

The described results together with the earlier obtained [2] data lead to the conclusion that the presence of the methoxyl group in the meta-position with respect to the point of ring B closure excludes the possibility of a one-step realization of the investigated conversion. In these cases the tricyclic methoxy ketones can be obtained by way of separate closure of rings B and C.





EXPERIMENTAL

β-(o-Tolyl)ethylmalonic Ester (III, R = o-CH_3). This ester was obtained earlier by Wessely and Wang [5], who gave only the boiling point of the compound. β-(o-Tolyl)ethyl bromide (90 g), obtained by the method of Shorygin and Shorygina [6], was condensed with the sodio derivative of malonic ester, prepared from 110 g of this ester and 13 g of sodium in 210 ml of anhydrous alcohol. After two vacuum distillations there was obtained 85 g (67.7 %) of colorless oil with b.p. 171-176° at 5 mm (in the literature [5] the indicated b.p. is 185-187° at 9 mm).

d_4^{20} 1.0550, n_D^{20} 1.4930. MR_D 75.82. $C_{16}H_{22}O_4$. Calculated 75.79.

0.1160 g sub.: 0.2920 g CO_2; 0.0856 g H_2O. 0.1054 g sub.: 0.2670 g CO_2; 0.0782 g H_2O. Found %: C 68.65, 69.11; H 8.20, 8.24. $C_{16}H_{22}O_4$. Calculated %: C 69.06; H 7.91.

β-(o-Anisyl)ethylmalonic Ester (III, R = o-CH_3O). β-(o-Anisyl)ethylbbromide (143.3 g) was added with stirring to a solution of the sodio derivative of malonic ester, prepared from 160 g of malonic ester and 23 g of sodium in 270 g of anhydrous alcohol. The mixture was boiled for 3 hours, after which the greater part of the alcohol was distilled off, to the cooled solution was added hydrochloric acid-acidified water, the product was dissolved in ether, the solution was washed with water, and then dried over anhydrous sodium sulfate. Vacuum distillation gave 134 g (68.4%) of colorless oil:

B.p. 204-206° (15 mm), d_4^{20} 1.0974, n_D^{20} 1.4966, MR_D 78.33. $C_{16}H_{22}O_5$. Calculated 77.43.
0.1017 g sub.: 0.2444 g CO_2; 0.0696 g H_2O. Found %: 65.54; H 7.64. $C_{16}H_{22}O_5$. Calculated %: C 65.31; H 7.48.

[β-(o-Tolyl)ethyl]-(3-chlorocrotyl)malonic Ester (IV, R = o-CH_3). To a solution of the sodio ester derivative (III, R = o-CH_3), prepared from 83 g of the ester and 7.3 g of sodium in 140 ml of anhydrous alcohol, with water cooling and stirring was added 43 g of freshly distilled 1,3-dichloro-2-butene. The mixture was boiled for 4 hours, after which part of the alcohol was distilled off, to the residue was added hydrochloric acid-acidificd water, the product was dissolved in ether, the solution was washed with water, and then dried over sodium sulfate. Vacuum distillation gave 99.3 g (90.75%) of viscous, light yellow liquid:

B.p. 192-196° (2 mm), d_4^{17} 1.0989, n_D^{17} 1.5080, MR_D 99.42. $C_{20}H_{27}O_4Cl$. Calculated 98.66.
0.1033 g sub.: 0.0416 g AgCl. 0.1047 g sub.: 0.0408 g AgCl. Found %: Cl 9.96, 9.64. $C_{20}H_{27}O_4Cl$. Calculated %: Cl 9.68.

[β-(o-Anisyl)ethyl]-(3-chlorocrotyl)malonic Ester (IV, R = o-CH_3O). In similar manner the condensation of 40 g of the dichlorobutene with the sodio ester derivative (III, R = o-CH_3O), prepared from 70 g of the ester and 5.5 g of sodium in 70 ml of anhydrous alcohol, gave 79.2 g (87%) of viscous, almost colorless oil:

B.p. 230-236° (14 mm), d_4^{20} 1.1229, n_D^{20} 1.5090, MR_D 101.70. $C_{20}H_{27}O_5Cl$. Calculated 100.31.
0.0922 g sub.: 0.0379 g AgCl. 0.1231 g sub.: 0.0470 g AgCl. Found %: Cl 9.49, 9.45. $C_{20}H_{27}O_5Cl$. Calculated %: Cl 9.28.

[β-(o-Tolyl)ethyl]-(3-chlorocrotyl)malonic Acid (V, R = o-CH_3). A mixture of 455 ml of 90% alcohol, 33 g of sodium hydroxide and 95.5 g of the disubstituted malonic ester (IV, R = o-CH_3) was boiled under reflux for 4 hours, after which the alcohol was completely removed by distillation, and the cooled alkaline solution was acidified with hydrochloric acid. The separated viscous oil, gradually crystallizing, was dissolved in ether, and the solution was washed with water and dried over sodium sulfate. The crystalline substance remaining after ether removal was washed with benzene, in which it is almost insoluble. The yield of colorless crystals with m.p. 173-174° was 71 g (87.76%).

0.1022 g sub.: 0.0482 g AgCl. 0.1006 g sub.: 0.0466 g AgCl. Found %: Cl 11.67, 11.46. $C_{16}H_{19}O_4Cl$. Calculated %: Cl 11.43.

[β-(o-Anisyl)ethyl]-(3-chlorocrotyl)malonic Acid (V, R = o-CH_3O). In the above described manner the saponification of 79 g of the ester (IV, R = o-CH_3O) with a solution of 25 g of sodium hydroxide in 250 ml of moist alcohol gave 63.5 g (94.2%) of benzene-washed colorless crystals with m.p. 161-162°.

0.1023 g sub.: 0.0438 g AgCl. 0.1025 g sub.: 0.0448 g AgCl. Found %: Cl 10.59, 10.81. $C_{16}H_{19}O_5Cl$. Calculated %: Cl 10.87.

α-(3-Chlorocrotyl)-γ-(o-tolyl)butyric Acid (II, R = o-CH_3). Twenty grams of the disubstituted malonic acid (V, R = o-CH_3) was decarboxylated by heating in a distilling flask until the evolution of carbon dioxide gas had ceased. Distillation of the obtained oil gave 16 g (93.2%) of substance with b.p. 204-205° at 3 mm, completely crystallizing in the receiver. M.p. 51-52°.

0.1033 g sub.: 0.0558 g AgCl. 0.1010 g sub.: 0.0554 g AgCl. Found %: Cl 13.36, 13.57. $C_{15}H_{19}O_2Cl$. Calculated %: Cl 13.32.

α-(3-Chlorocrotyl)-γ-(o-anisyl)butyric Acid (II, R = o-CH_3O). The decarboxylation of 30 g of the dibasic acid (V, R = o-CH_3O) gave 24.1 g (92.85%) of viscous, light yellow oil:

B.p. 210-215° (10 mm), d_4^{20} 1.1615, n_D^{20} 1.5363, MR_D 75.88. $C_{15}H_{19}O_3Cl$. Calculated 75.44.
0.1029 g sub.: 0.0497 g AgCl. Found %: Cl 12.43. $C_{15}H_{19}O_3Cl$. Calculated %: Cl 12.56.

3-Keto-8-methyl-1,2,3,9,10,10a-hexahydrophenanthrene (I, R = 8-CH_3). To 7 g of the acid (II, R = o-CH_3) with ice cooling and stirring was gradually added 35 ml of sulfuric acid (d 1.78). The mixture was let stand at room temperature until foaming had ceased, caused by the evolution of hydrogen chloride (about a half hour), after which the mixture was heated for 5 hours on the water bath (60-75°) in a stream of carbon dioxide gas, and then let stand overnight. When mixed with ice water a crystalline substance separated, which was filtered, rubbed with an excess of 10% sodium hydroxide solution, again filtered, washed with water, and dried. Recrystlalization of the crude product (4 g) from alcohol gave 3.5 g (62.95%) of colorless crystals with m.p. 157-158°.

0.1032 g sub.: 0.3207 g CO_2, 0.0745 g H_2O. 0.1053 g sub.: 0.3214 g CO_2. 0.0758 g H_2O. Found %: C 84.75, 84.92; H 8.02, 7.99. $C_{15}H_{16}O$. Calculated %: C 84.90; H 7.55.

The 2,4-dinitrophenylhydrazone, obainted from 0.3 g of the ketone (I, R = 8-CH_3) and 0.26 g of dinitrophenylhydrazine in alcohol, after recrystallization from chloroform-alcohol mixture, had m.p. 223-224°.

0.0326 g sub.: 4.5 ml N_2 (20°, 678 mm). Found %: N 14.47. $C_{21}H_{20}O_4N_4$. Calculated %: N 14.29.

3-Hydroxy-8-methylphenanthrene (VI). One gram of the ketone (I, R = 8-CH_3) was dehydrogenated by heating with 0.3 g of sulfur at 180-215° to cessation of hydrogen sulfide evolution (about a half hour). The crystallized dehydrogenated product was dissolved with cooling in 5% alkali, after which the solution was filtered and acidified. Recrystallization of the filtered and dried substance from alcohol (boiled with carbon) gave fluffy, light cream crystals with m.p. 144-145°. Yield 0.5 g (50.9%).

0.0937 g sub.: 0.2961 g CO_2; 0.0520 g H_2O. 0.0907 g sub.: 0.2849 g CO_2; 0.0510 g H_2O. Found %: C 86.18; 86.54; H 6.16, 6.28. $C_{15}H_{12}O$. Calculated %: C 86.54; H 5.77.

The orange-yellow picrate, obtained from alcohol, had m.p. 180°.

Action of Sulfuric Acid on α-(3-Chlorocrotyl)-γ-(o-anisyl)-butyric Acid. Three grams of the acid (II, R = o-CH_3O) was treated with 18 ml of sulfuric acid (d 1.78) under the conditions described above for the nuclear methylated acid. The mixture was heated in a carbon dioxide stream for 3 hours at 60°. When the red solution was mixed with ice water a dark colored waxy substance separated. This substance failed to dissolve in ether, but dissolved completely on rubbing with a large amount of water, forming a light purple opalescent solution. The substance dissolved immediately in alkali. Any neutral products were completely absent.

2-(3-Chlorocrotyl)-5-methoxy-1-tetralone (VII). To a solution of 10 g of the acid (II, R = o-CH_3O) in 18 ml of dry benzene was added in small portions 7.3 g of phosphorus pentachloride. After vigorous reaction had ceased the greater part of the benzene and the phosphorus oxychloride formed in the reaction were distilled off on the boiling water bath. The rest of the benzene and phosphorus oxychloride was removed in vacuo, and the gradually raised temperature of the mixture was brought to 180°. At this temperature decomposition set in with the copious evolution of hydrogen chloride. After gas evolution had ceased the residue was dissolved in ether, the solution washed with alkali, then with water, and finally dried over sodium sulfate. Vacuum distillation gave 5.7 g (60.9%) of yellowish viscous oil with b.p. 190° (8 mm).

0.1040 g sub.: 0.0527 g AgCl. 0.1022 g sub.: 0.0565 g AgCl. Found %: Cl13 97, 13.68. $C_{15}H_{17}O_2Cl$. Calculated %: Cl 13.42.

This ketone, similar to its 7-methoxy isomer [2], fails to form the semicarbazone, apparently due to the fact that it is an o,o' - substituted cyclohexanone.

3-Keto-8-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (I, R = 8-CH_3O). The substituted tetralone (VII) (3.4 g) with water cooling was treated with 8 ml of sulfuric acid (d 1.74). The mixture stood at room temperature for 24 hours. When the red solution was mixed with ice water a product separated, which partially crystallized. The substance was dissolved in ether, the solution washed with alkali and water, and dried over sodium sulfate. The crystalline product remaining after ether removal was recrystallized from alcohol. The yield of colorless crystals with m.p. 111-112° was 1.4 g (47.7%).

0.1000 g sub.: 0.2904 g CO_2; 0.0658 g H_2O. 0.1006 g sub.: 0.2911 g CO_2; 0.0664 g H_2O. 0.2220 g sub.: 0.2270 g AgI. Found %: C 79.20, 78.94; H 7.31, 7.33, CH_3O 13.51. $C_{14}H_{13}O(OCH_3)$. Calculated %: C 78.94; H 7.02; CH_3O 13.54.

The 2,4-dinitrophenylhydroazone, obtained from 0.35 g of the methoxy ketone and 0.25 g of phenylhydrazine in alcohol, after recrystallization from a chloroform-alcohol mixture, melted at 233°.

0.1004 g sub.: 13.2 ml N_2 (23.5°, 672 mm). Found %: N 13.39, $C_{21}H_{20}O_5N_4$. Calculated %: N 13.72.

3-Hydroxy-8-methoxyphenanthrene (VIII). The methoxy ketone (3 g) was dehydrogenated by heating with 1 g of sulfur (180-215° 1 hour). The crystaline dehydrogenation product was dissolved in alkali, the solution filtered, acidified, the precipated substance washed with water, and dried. Recrystallization of the product from methyl alcohol (boiling with carbon) and from water gave 1.7 g (57.8%) of colorless crystals with m.p. 170-171°.

0.0621 g. sub.: 0.1822 g CO_2; 0.0298 g H_2O. 0.0640 g sub.: 0.1882 g CO_2; 0.0318 g H_2O. Found %: C 80.00, 80.19; H 5.33, 5.52. $C_{15}H_{12}O_2$. Calculated %: C 80.35; H 5.35.

3,8-Dimethoxyphenanthrene (IX). To a solution of 0.5 g of 3-hydroxy-8-methoxyphenanthrene in 18 ml of 2% sodium hydroxide, heated on the water bath, was added dropwise 0.8 g of dimethyl sulfate. The mixture was heated for 15 minutes, after which 15 ml of 4% sodium hydroxide solution was added and the heating continued another 15 minutes. After cooling, the crystalline product was filtered and washed with water. The yield of methyl alcohol recrystallized colorless crystals with m.p. 116-117° was 0.4 g (75.4%) (the literature [4] for 3,8-dimethoxyphenanthrene gives m.p. 117°).

SUMMARY

1. The influence of the methyl and methoxyl groups, found in the ortho-position of the aromatic nucleus, on the sulfuric acid hydrolysis and double cyclization of α-(3-chlorocrotyl)-γ-phenylbutyric acids was investigated.

2. It was shown that the methyl group fails to exert substantial influence on the course of the investigated transformation; the cyclization product – 3 keto-8-methylhexahydrophenanthrene – is obtained in a yield of the same order as that of the unsubstituted ketone and its other methyl homologs.

3. The presence of a methoxyl group in the ortho-position excludes the possibility of realizing the investigated transformation in one stage; in this case, as in the case where the same group is present in the para-position, the tricyclic methoxy ketone can be obtained by way of separate closure of rings B and C.

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* Consultants Bureau Translation, p. 289.

** Consultants Bureau Translation, p. 1277.

*** Consultants Bureau Translation, p. 979.

boiling with carbon) and then water gave 1.6 g (47.5%) of colorless crystals with m.p. [illegible]

[illegible] g CO₂; [illegible] g H₂O; [illegible]. Found %: C [illegible]; H [illegible]. $C_{[illegible]}H_{12}O_3$. Calculated %: C [illegible]; H [illegible].

[illegible] To a solution of [illegible] g of [illegible] in [illegible] ml of [illegible] hydroxide, heated on the water bath, was added dropwise [illegible] g of [illegible]. The [illegible] washed [illegible], after which [illegible] ml of [illegible] was added and the heating continued for [illegible] minutes. After cooling, the crystalline product was filtered and washed with water. The [illegible] recrystallized colorless crystals with m.p. [illegible] was [illegible] g ([illegible]%) (the literature [4] for [illegible] gives m.p. [illegible]).

SUMMARY

1. The influence of the methyl and methoxyl groups, found in the ortho-position of the aromatic nucleus, on the nitrile acid hydrolysis and double cyclization of [illegible] was investigated.

2. It was shown that the methyl group fails to exert substantial influence on the course of the investigated transformation; the cyclization product [illegible] was obtained in a yield about the same as that of the unsubstituted [illegible] and its other methyl homologs.

3. The presence of a methoxyl group in the ortho-position excludes the possibility of effecting the investigated transformation in one stage. In this case, as in the case where the same group is present in the para-position, the [illegible] can be obtained by way of separate stages of [illegible] and C[illegible]

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* Consultants Bureau Translation, p. [illegible]

** Consultants Bureau Translation, p. [illegible]

*** Consultants Bureau Translation, p. [illegible]

PREPARATION OF SOME 3-ARYLOXAZOLIDINES

Yu. K. Yurev, L. F. Gorin and A. N. Vysokosov

The condensation of N-(β-hydroxyethyl)arylamines with aldehydes, leading to 3-aryloxazolidines, up to now has been studied only for the examples N-(β-hydroxyethyl)aniline and N-(β-hydroxyethyl)-p-phenetidine.

Thus, Bergmann, Ulpts and Camacho [1], on heating these arylethanolamines with formalin and with benzaldehyde obtained 3-phenyloxazolidine, 3-p-phenetyloxazolidine and 2-phenyl-3-p-phenetyloxazolidine. 3-Phenyloxazolidine was also described by Kon and Roberts [2]. In 1952 Zimkin and Bergmann [3] described the preparation of 3-phenyloxazolidine, and also 2-methyl-, 2-ethyl-, 2-propyl-, 2-(2'-ethyl)hexyl- and 2,3-diphenyloxazolidine.

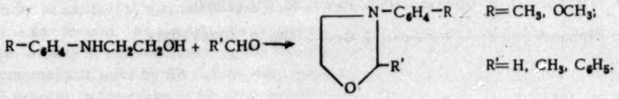
The formation of the oxazolidine cycle proceeds under mild conditions and depends but slightly on the structure of the aldehyde. Thus, the condensation of N-(β-hydroxyethyl)aniline with acetaldehyde proceeds at room temperature in ether solution; with other aldehydes the formation of the oxazolidines proceeds under the removal of the reaction water by distillation with benzene.

In their work on the synthesis of N-substituted 2-aryl-oxazolidines, Ushenko, Baranov and Gorizdra [4] introduced into the reaction with N-(β-hydroxyethyl)aniline the aldehydes benzaldehyde, o-chlorobenzaldehyde and also m-nitrobenzaldehyde, and obtained the corresponding 2,3-diphenyloxazolidine, 2-o-chlorophenyl-3-phenyloxazolidine and 2-m-nitrophenyl-3-phenyloxazolidine. Petrov and Gosteva [5] obtained 2-furyl-3-phenyloxazolidine by pouring together over 10 minutes molar amounts of furfural and N-(β-hydroxyethyl) aniline in the presence of 1 g of potash. The attempts of Kiprianov and Rozhkova [6] to condense N-(β-hydroxyethyl) aniline with ketones gave negative results.

In the present work it was shown by us that N-(β-hydroxyethyl)-o-toluidine, N-(β-hydroxyethyl)-p-toluidine and N-(β-hydroxyethyl)-p-anisidine condense with benzaldehyde in the same manner as N-(β-hydroxyethyl)aniline [3,4]. When the water was removed from the reaction mixture by distillation with benzene there were obtained in good yields 2-phenyl-3-p-tolyloxazolidine and 2-phenyl-3-p-anisyloxazolidine, and in lower yield 2-phenyl-3-o-tolyloxazolidine.

From the mixture of N-(β-hydroxyethyl)-p-toluidine with acetaldehyde in ether after one day standing at room temperature there was obtained 2-methyl-3-p-tolyloxazolidine. It should be mentioned that N-(β-hydroxyethyl)o-toluidine fails to react with acetaldehyde under these conditions, while in the reaction with benzaldehyde the 2-phenyl-3-o-tolyloxazolidine is obtained in half the yield of the 2-phenyl-3-p-tolyloxazolidine.

The heating of N-(β-hydroxyethyl)-p-toluidine with 30% formalin led to the formation of 3-p-tolyloxazolidine.



EXPERIMENTAL

3-p-Tolyloxazolidine. A mixture of 15 g of N-(β-hydroxyethyl)-p-toluidine and 10 ml of 30% formalin was heated for 1 hour on the water bath under reflux. Cooling of the reaction mixture gave crystals, which were filtered and washed with ether. Recrystallization from petroleum ether gave 14.7 g of 3-p-tolyloxazolidine (89.5%) with m.p. 61.5°. Not described in the literature.

Found %: N 8.67, 8.59. $C_{10}H_{13}ON$. Calculated %: N 8.59.

2-Methyl-3-p-tolyloxazolidine. Fifteen grams of N-(β-hydroxyethyl)-p-toluidine was mixed with 4.6 g of acetaldehyde in 50 ml of anhydrous ether and let stand 24 hours. After removing the water the ether solution was dried over calcined potash. After distilling off the ether the residue was vacuum distilled to give: 1.2 g of fraction with m.p. 42°, being unchanged N-(β-hydroxyethyl)-p-toluidine, and 12.3 g (80% of the theoretical, based on reacted ethanol-p-toluidine) of an oil with slight odor, being 2-methyl-3-p-tolyloxazolidine. Not described in the literature.

B.p. 121.5-122° (9 mm), n_D^{20} 1.5540, d_4^{20} 1.0484, MR_D 54.18. $C_{11}H_{15}ON\overline{|}_3$. Calculated 53.86.
Found %: N 8.21, 8.41. $C_{11}H_{15}ON$. Calculated %: N 7.90.

2-Phenyl-3-*p*-tolyloxazolidine. A mixture of 30 g of N-(β -hydroxyethyl)-*p*-toluidine and 21.5 g of benzaldehyde in 100 ml of benzene was boiled for 6 hours until the water present in the mixture was completely removed. Amount of removed water 3 g. After distilling off the benzene the residue crystallized to give 43.2 g (91%) of crude 2-phenyl-3-*p*-tolyloxazolidine, melting at 61°. After recrystallization from petroleum ether the substance melted at 71° and was pure 2-phenyl-3-*p*-tolyloxazolidine. Not known in the literature.

Found %: N 5.81, 5.86. $C_{16}H_{17}ON$. Calculated %: N 5.85.

2-Phenyl-3-*o*-tolyloxazolidine. A mixture of 15 g of N-(β -hydroxyethyl)-*o*-toluidine and 10.8 g of benzaldehyde in 100 ml of benzene was boiled for 8 hours until all of the water was removed. About 1g of water was collected. After distilling off the benzene the residue (23 g of oil) was vacuum distilled through a fractionation column to give the 2-phenyl-3-*o*-tolyloxazolidine. Yield 6.5 g (38%). Not described in the literature

B.p. 147-148° (2 mm), n_D^{20} 1.5853, d_4^{20} 1.1032, MR_D 72.76. $C_{16}H_{17}ON\overline{F}_3$. Calculated 72.27.
Found %: N 6.18, 6.29. $C_{16}H_{17}ON$. Calculated %: N 5.86.

2-Phenyl-3-*p*-anisyloxazolidine. A mixture of 8.3 g of N-(β -hydroxyethyl)-*p*-anisidine and 5.3 g of benzaldehyde in 100 ml of benzene was boiled for 6 hours to distill off the water. Amount of collected water 0.9 g. The residue crystallized after removal of the benzene by distillation. After recrystallization from petroleum ether the substance melted at 60-60.5° and was 2-phenyl-3-*p*-anisyloxazolidine. Yield 10.2 g (80%). Not described in the literature.

Found %: N 5.67, 5.68. $C_{16}H_{17}O_2N$. Calculated %: N 5.45.

SUMMARY

1. The unknown 2-methyl-3-*p*-tolyloxazolidine, 2-phenyl-3-*p*-tolyloxazolidine, 2-phenyl-3-*o*-tolyloxazolidine and 2-phenyl-3-*p*-anisyloxazolidine were prepared.

2. N-(β -Hydroxyethyl)-*o*-toluidine, in contrast to N-(β -hydroxyethyl)-*p*-toluidine, fails to react with acetaldehyde at room temperature in ether and in the reaction with benzaldehyde gives 2-phenyl-3-*o*-tolyloxazolidine in one half the yield of 2-phenyl-3-*p*-tolyloxazolidine.

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β-LACTONES AND β-LACTONO ACIDS

XI. REFORMATSKY REACTION WITH BROMOMALONIC ESTER

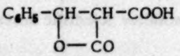
II. BENZALMALONO-β-LACTONE

N. S. Wulfson

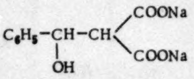
In one of the previous communications [1], on the example of condensing acetone with mixed malonic acetic anhydride, it was shown by us that the intermediate product in the formation of the β-lactone of isopropylidenemalonic acid is the mixed anhydride of β-hydroxyisopropylmalonic and acetic acids. This compound proved to be extremely unstable and could not be isolated in the pure form. We judged its formation by means of indirect reactions.

In another of our papers [2] it was shown that in the Reformatsky reaction between benzaldehyde and bromomalonic ester the ester of β-hydroxybenzalmalonic acid is formed in the first step, which is easily dehydrated, and the ester of benzalmalonic acid is isolated as the final reaction product. However, under mild saponification of the reaction product with an alcoholic sodium hydroxide solution we obtained the sodium salt, the analysis of which well agreed with that calculated for the salt of β-hydroxybenzylmalonic acid.

On the basis of earlier expressed representations as to the mechanism for the formation of β-lactono acids [1], we postulated that in the reaction of the sodium salt of the β-hydroxydicarboxylic acid with acetyl chloride the mixed anhydride of β-hydroxybenzylmalonic and acetic acids should be obtained, which under the proper conditions should lead to the formation of the β-lactone of benzalmalonic acid (I).



(I)



(II)

Actually, on adding 2 moles of acetyl chloride to a suspension of the sodium salt (obtained by mild saponification of the condensation product from bromomalonic ester and benzaldehyde in the presence of zinc) in anhydrous ether the β-lactone of benzalmalonic acid (I) was isolated, identical with the product described in the literature [3] and obtained by us in earlier studies [1,4].

It was shown by us earlier [1] that in the action of acetyl chloride on the silver salt of benzalmalonic acid the β-lactono acid (I) is not formed. As a result, the preparation of the β-lactone of benzalmalonic acid described in this paper confirms the validity of our conclusion on the formation of the ester of β-hydroxybenzylmalonic acid from benzaldehyde and bromomalonic ester by the Reformatsky reaction. In addition, the described experiments again support the validity of the scheme, proposed by us for the reaction mechanism involved in the formation of β-lactono acids.

EXPERIMENTAL

Preparation of the Sodium Salt of β-Hydroxybenzylmalonic Acid. (II). In a 100 ml round-bottomed flask with stirrer and reflux condenser was boiled a mixture of 10.6 g of freshly distilled (in vacuo) benzaldehyde, 24 g of bromomalonic ester, 50 ml of dry benzene and 6.55 g of zinc turnings (etched with 10 % hydrochloric acid, washed with water, methanol and acetone, dried, and heated with an iodine crystal). The clear colorless solution gradually became cloudy and turned brown. Reaction was not too vigorous, but considerable zinc dissolved. The mixture was heated with stirring for 3 hours. Toward the end of heating a fairly copious, white, amorphous precipitate was obtained. After cooling the reaction mass was decomposed with 100 ml of 10% sulfuric acid. There remained 0.6 g of unreacted zinc. The benzene solution was washed twice with 50 ml portions of sodium bisulfite solution, 10% soda solution, repeatedly with water to neutrality of the wash liquors, and dried over magnesium sulfate. To the benzene solution was added 100 ml of 5% alcoholic sodium hydroxide solution and the whole let stand overnight at room temperature. The precipitate was filtered, washed with alcohol and recrystallized from 70% alcohol. Yield of sodium salt (II) 16 g.

0.0770, 0.0476, 0.1615 g sub.: 0.0432, 0.026, 0.0895 g Na_2SO_4. Found %: Na 18.18, 17.85, 17.94. $C_{10}H_8O_5Na_2$. Calculated %: Na 18.07.

Preparation of Benzalmalono-β-Lactone (I). To a suspension of 5.08 g of the sodium salt (II) in 50 ml of dry ether was added dropwise at temperature not over 25° and with stirring 3.14 g of acetyl chloride. Stirring was maintained for 15 minutes, the sodium chloride precipitate was filtered, washed with dry ether, and the combined ether solutions let stand overnight. The ether was removed in vacuo, while the residue was recrystallized from acetone-benzene mixture. Yield 2.7 g (70.3%, based on sodium salt (II), or 47%, based on benzaldehyde). M.p. 145-146°. The mixed melting point with the β-lactone of benzalmalonic acid, obtained by other methods [1,4], failed to be depressed.

0.0752 g sub.: (dissolved in 15 ml of 70% alcohol): 3.87 ml 0.1 N NaOH. $C_{10}H_8O_4$. Calculated for monobasic acid: 3.92 ml NaOH.

SUMMARY

The reaction of acetyl chloride with the sodium salt, formed in the saponification of the condensation product from benzaldehyde and bromomalonic ester (Reformatsky reaction), gave the β-lactone of benzalmalonic acid. In that way it was shown that the Reformataky reaction between benzaldehyde and bromomalonic ester gives the ester of β-hydroxybenzylmalonic acid. In addition, it was again experimentally confirmed that the intermediate product in the reaction for the formation of β-lactono acids is the mixed anhydride of β-hydroxyalkyl (ovaryl) malonic and acetic acids.

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* Consultants Bureau Translation, p. 449.

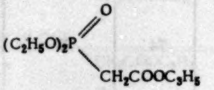
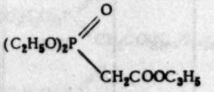
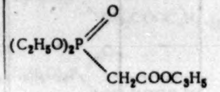
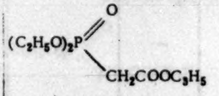
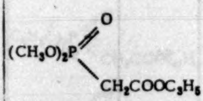
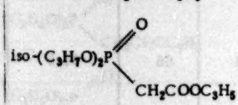
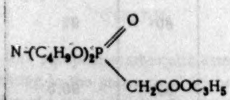
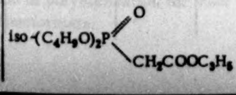
POLYMERIZATION OF SOME UNSATURATED ESTERS OF PHOSPHONOCARBOXYLIC ACIDS

Gilm Kamai and V. A. Kukhtin

In an earlier published paper [1] it was shown by us that the allyl esters of acetylphosphinic and benzoylphosphinic acids can be polymerized when heated, forming gel polymers. These same esters also readily copolymerize with methyl methacrylate, forming fire-resistant copolymers.

The synthesis of some new unsaturated esters of phosphonocarboxylic acids and the results of studying their polymerization tendency are described in the present paper.

TABLE 1

Exp. No.	Ester	Organophosphorus addition (in %)	Time of polymerization (in hours)	Brinell Hardness (kg/sq. mm)	Heat resistance (in °C)	Specific impact viscosity (kg · cm/sq. cm)	Clarity (in %)
1	 $(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	5	7.5	11.2	88	–	–
2	 $(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	10	9	10.4	74	12	91.5
3	 $(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	15	12	11.9	62	–	91.5
4	 $(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	20	16	7.4	49	16	89.5
5	 $(CH_3O)_2P(=O)CH_2COOC_3H_5$	15	16	11.2	65	12.5	91.7
6	 $iso\text{-}(C_3H_7O)_2P(=O)CH_2COOC_3H_5$	15	18	12.3	72	11.4	91.5
7	 $N\text{-}(C_4H_9O)_2P(=O)CH_2COOC_3H_5$	15	17	12.9	63	13.3	92.4
8	 $iso\text{-}(C_4H_9O)_2P(=O)CH_2COOC_3H_5$	15	20	14	67	13	91.5

We synthesized the unsaturated esters of phosphonocarboxylic acids by the usual methods [2,3]. Some of the physical constants of the obtained compounds are given in Table 3.

The esters of phosphonoacetic acid with one allyl group at the carbon (Table 3, Compounds 1-5) showed slight inclincation to polymerize. Only the first three esters under prolonged heating with benzoyl peroxide form low-molecular polymers (with n = 2-4 for the degree of polymerization). The polymerization of these esters was run at 60-70° for a period of 200 hours with the addition of 1% (by weight) of benzoyl peroxide.

We prepared a number of copolymers of these esters with methyl methacrylate and studied their properties. All of the obtained copolymers are hard, transparent, colorless or slightly yellow resins. The copolymers have a low-hardness and poor heat resistance. Copolymers, containing 15 and 20% of the organophosphorus component, are quickly self-extinguishing after removal of the flame.

The physical and mechanical properties of the copolymers are given in Table 1.

TABLE 2

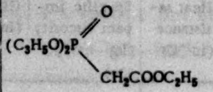
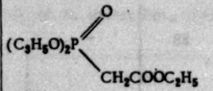
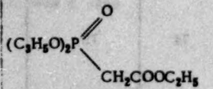
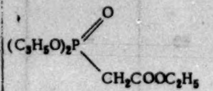
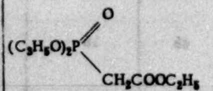
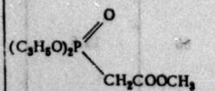
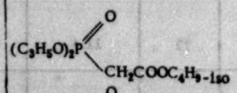
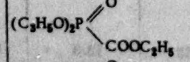
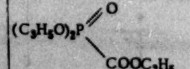
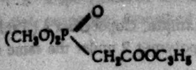
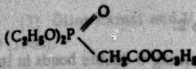
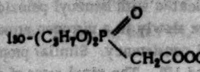
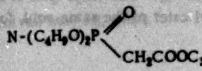
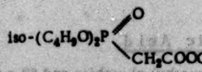
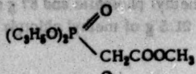
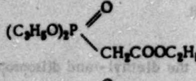
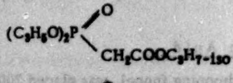
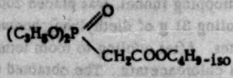
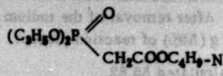
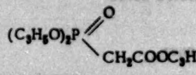
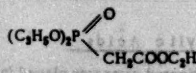
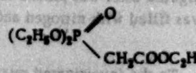
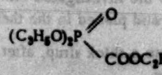
Exp. No.	Ester	Organophosphorus addition (in %)	Time of polymerization (in hours)	Brinell Hardness (kg/sq. mm)	Heat resistance (in °C)	Specific impact viscosity (kg · cm/sq. cm)	Clarity (in %)
1	 O $(C_3H_5O)_2P$ $CH_2COOC_2H_5$	10	20	9	65	91.2	10.3
2	 O $(C_3H_5O)_2P$ $CH_2COOC_2H_5$	20	28	8.9	74	92	7.8
3	 O $(C_3H_5O)_2P$ $CH_2COOC_2H_5$	30	37	4.7	48	91.7	12
4	 O $(C_3H_5O)_2P$ $CH_2COOC_2H_5$	40	46	–	–	–	–
5	 O $(C_3H_5O)_2P$ $CH_2COOC_2H_5$	50	53	–	–	–	–
6	 O $(C_3H_5O)_2P$ CH_2COOCH_3	25	26	8	56	92	–
7	 O $(C_3H_5O)_2P$ $CH_2COOC_4H_9$-iso	25	20	10.3	65	91.5	6.4
8	 O $(C_3H_5O)_2P$ $COOC_2H_5$	20	11	12.1	60	92	–
9	 O $(C_3H_5O)_2P$ $COOC_2H_5$	30	17	4.5	36	90.5	10.9

TABLE 3

Exp. No.	Ester	Boiling point at pressure (in mm)	n_D^{20}	d_0^{20}	P content in %	
					Calculated	Found
1	 $(CH_3O)_2P(O)CH_2COOC_3H_5$	114 - 114.5 (2)	1.4505	1.2064	14.83	14.53
2	 $(C_2H_5O)_2P(O)CH_2COOC_3H_5$	157 - 158 (10)	1.4426	1.1203	13.54	13.87
3	 $iso\text{-}(C_3H_7O)_2P(O)CH_2COOC_3H_5$	152 - 153 (6)	1.4357	at 15° 1.0520	11.71	11.60
4	 $N\text{-}(C_4H_9O)_2P(O)CH_2COOC_3H_5$	146 - 147.5 (1)	1.4470	at 15° 1.0492	10.59	10.42
5	 $iso\text{-}(C_4H_9O)_2P(O)CH_2COOC_3H_5$	154 - 156 (4)	1.4438	at 15° 1.0356	10.59	10.21
6	 $(C_3H_5O)_2P(O)CH_2COOCH_3$	128 - 129 (3)	1.4578	1.1478	13.22	13.17
7	 $(C_3H_5O)_2P(O)CH_2COOC_2H_5$	133 - 134 (3)	1.4521	1.1186	–	–
8	 $(C_3H_5O)_2P(O)CH_2COOC_3H_7\text{-}iso$	150 - 151 (5)	1.4545	1.0983	11.81	11.94
9	 $(C_3H_5O)_2P(O)CH_2COOC_4H_9\text{-}iso$	130 - 131 (1)	1.4560	1.0850	11.21	11.29
10	 $(C_3H_5O)_2P(O)CH_2COOC_4H_9\text{-}N$	142 - 143 (1.5)	1.4552	1.0801	11.21	11.39
11	 $(C_3H_5O)_2P(O)CH_2COOC_3H_5$	165 - 166 (9)	1.4711	1.0967	11.82	11.69
12	 $(C_3H_5O)_2P(O)CH_2COOC_2H_3$	107 - 108 (2)	1.4576	1.0512	12.58	12.61
13	 $(C_2H_3O)_2P(O)CH_2COOC_2H_3$	103 - 104 (2.5)	1.4340	1.1190	13.93	14.04
14	 $(C_3H_5O)_2P(O)COOC_2H_5$	126 - 127 (3)	1.4490	1.1204	–	–

The phosphonocarboxylic esters with two allyl groups at the phosphorus (Table 3, Compounds 6-10 and 14) under heating in the presence of 1% benzoyl peroxide form transparent gel polymers, insoluble in organic solvents. The duration of polymerization for these esters at 70° was 70-100 hours for the phosphonoacetates and 40-50 hours for the phosphonoformate.

We prepared a number of copolymers of these esters with methyl methacrylate and studied their properties. The copolymers, containing 10 and 20% by weight of the phosphonoacetate, possess reduced inflammability.

With increase in the phosphorus content the hardness and heat resistance of the copolymers are reduced. In contrast to the esters with one allyl group, the esters with two allyl groups markedly lower the specific impact viscosity.

The obtained copolymers are poorly soluble in organic solvents. Thus, for example, Copolymer 1 (Table 2) in 24 hours at room temperature dissolves in acetone to the extent of only 12.1%, and Copolymer 2 under the same conditions to the extent of 13.8%.

The physical and mechanical properties of the copolymers are given in Table 2.

The allyl ester of diallylphosphonoacetic acid (Table 3, Compound 11), containing 3 double bonds in its molecule, strongly differs from the other esters in its polymerization properties. When heated with benzoyl peroxide in the air it quickly turns dark red and fails to polymerize. The color changes much more slowly in a nitrogen atmosphere; however, here also polymerization fails to occur and the product retains its original consistency. Similar properties are also possessed by the vinyl ester of diallylphosphonoacetic acid (Table 3, Compound 12). The vinyl ester of diethylphosphonoacetic acid (Table 3, Compound 13) polymerizes in the same way as the allyl ester of the same acid, forming a low-molecular sirupy polymer.

EXPERIMENTAL

Synthesis of the Allyl Ester of Dimethylphosphonoacetic Acid.

In a round-bottomed flask fitted with reflux condenser was placed 62 g of trimethyl phosphite and 67 g of allyl chloroacetate. The reaction flask was heated at 110-120° for 4 hours. In this time 21.5 g of methyl chloride was evolved (86%). After three distillations 22.5 g of substance was collected.

B.p. 114-114.5° (2 mm), d_0^{20} 1.2064, n_D^{20} 1.4505, MR_D 46.48; calculated 46.58.
Found %: P 14.53, 14.32. $C_7H_{13}O_5P$. Calculated %: P 14.83.

All of the other esters were obtained in similar manner, with the exception of the diethyl- and diisopropylphosphonoacetates.

Synthesis of the Allyl Ester of Diethylphosphonoacetic Acid.

In a 500 ml three-necked flask, fitted with reflux condenser, stirrer and dropping funnel, was placed 200 ml of dry ether, and 5.3 g of metallic sodium (as wire) was introduced. Then with cooling 31 g of diethylphosphorous acid was added, after which the reaction mass was heated on the water bath for 30 minutes. After cooling to room temperature, to the flask with reaction mixture was added with constant stirring 30 g of allyl chloroacetate. The obtained sodium chloride precipitate was coagulated by boiling with activated carbon for 1 hour. After removal of the sodium chloride and distilling off the solvent a 2-fold vacuum distillation of the residue gave 29 g (55%) of reaction product.

B.p. 157-158° (10 mm), d_0^{20} 1.1203, d_0^0 1.1387, n_D^{20} 1.4426, MR_D 56.28; calculated 55.82.
Found %: P 13.87, 13.93. $C_9H_{17}O_5P$. Calculated %: P 13.54.

The allyl ester of diisopropylphosphonoacetic acid was obtained in similar manner.

The physical constants of all of the obtained compounds are given in Table 3.

Polymerization of Unsaturated Esters of Phosphonocarboxylic Acids.

The polymerization experiments were run as follows. Four grams of the investigated ester was placed in a test tube and 0.04 g (1% by weight) of benzoyl peroxide was added. Then the test tube was filled with nitrogen and tightly stoppered with a rubber stopper. The polymerization was run in a thermostat at 70°.

The mixture of monomers was first placed in a flask with ground-glass stopper. To the investigated mixture was added 0.3% by weight of benzoyl peroxide, after which the flask was filled with nitrogen and placed in the thermostat.

Heating at 50-55° was maintained until the mixture of monomers was converted into a thick sirup, after which the obtained sirup was poured into the mold and heated at 50° to complete loss of fluidity.

Elevation of the temperature at this stage to above 50° can lead to the appearance of bubbles. As the copolymer hardened the temperature was gradually raised to 60-70° and it was maintained at this level until polymerization was complete.

SUMMARY

1. A number of new unsaturated esters of phosphonocarboxylic acids were synthesized and a study made of their polymerization tendency.

2. Copolymers of the unsaturated esters of phosphonocarboxylic acids with methyl methacrylate were prepared and their properties described.

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S. M. Kirov Kazan Chemical-Technological Institute

[illegible] Thus, for [illegible] to 12.5% and Compound 7 under the same conditions [illegible]

[illegible] Compound (1) [illegible] as shown in the [illegible]

[illegible] and the [illegible] its original [illegible]. Similar [illegible]

[illegible]

EXPERIMENTAL

Preparation of the Allyl Ester of [illegible]

[illegible] 13.2 g of triethyl phosphite and 21.1 g of allyl [illegible]. The [illegible] for 2 hours. In this case 11.0 g of methyl chloride was [illegible]

[illegible] calculated 30.55.

Found %: P [illegible]. Calculated %: P [illegible]

[illegible] with the exception of the diethyl- and dimethyl- [illegible]

Preparation of the Allyl Ester of Diethylphosphonoacetic Acid

[illegible] was placed [illegible] for 30 minutes. [illegible] 7.0 g of allyl [illegible]. The [illegible] for 1 hour. [illegible] gave 23 g (80%) of reaction product.

[illegible] d_4^{20} 1.1205 [illegible] calculated 55.62.

Found %: P [illegible]. Calculated %: P 13.12.

The allyl ester of diisopropylphosphonoacetic acid was obtained in similar manner.

The physical constants of all of the obtained compounds are given in Table 3.

Polymerization of Unsaturated Esters of Phosphonocarboxylic Acids

[illegible] was carried out as follows. Five grams of the investigated ester was placed in a [illegible] of benzoyl peroxide was added. Then the ampule was filled with nitrogen and [illegible] sealed. The polymerization was run in a thermostat at 70°.

[illegible] was then placed in a flask with ground-glass stopper. To the investigated [illegible] after which the flask was filled with nitrogen and placed in the thermostat.

[illegible] until the mixture of [illegible] was converted into a thick sirup, after which the [illegible] at 50° to complete loss of fluidity.

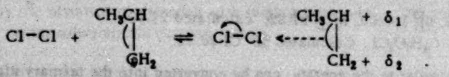
[illegible] to 100° [illegible] led to the appearance of bubbles. At the [illegible] polymerization was [illegible]

CONJUGATION REACTIONS OF HALOGEN ADDITION TO OLEFINS

III. ORDER OF ADDITION TO UNSYMMETRICAL OLEFINS

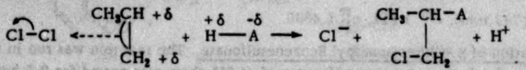
A. I. Titov and F. L. Maklyaev

The order of addition to olefins, for example to propylene, in conjugation reactions can be determined by considering the influence of substituents on the positive charge distribution in the intermediate complex of halogen with olefin [1,2].



$$Cl{-}Cl + \begin{array}{c} CH_3CH \\ \| \\ CH_2 \end{array} \rightleftharpoons \overset{\frown}{Cl{-}Cl} \dashleftarrow \begin{array}{c} CH_3CH + \delta_1 \\ \| \\ CH_2 + \delta_2 \end{array} \qquad (1)$$

Since the methyl group stabilizes the positive charge on the adjacent carbon, then $\delta_1 > \delta_2$ and the addition of anion A^- should proceed in the following order:



$$\overset{\frown}{Cl{-}Cl} \dashleftarrow \begin{array}{c} CH_3CH + \delta \\ \| \\ CH_2 + \delta \end{array} + \overset{+\delta}{H}{-}\overset{-\delta}{A} \longrightarrow Cl^- + \begin{array}{c} CH_3{-}CH{-}A \\ | \\ Cl{-}CH_2 \end{array} + H^+ \qquad (2)$$

Actually, our studies on the reaction of chlorine with propylene in either formic or acetic acid medium revealed that the reaction products are compounds of type $CH_2ClCHA{-}CH_3$, being respectively β-chloroisopropyl formate $CH_2Cl{-}CH(CH_3){-}OCHO$ and β-chloroisopropyl acetate $CH_2Cl{-}CH(CH_3)OCOCH_3$. To be sure, due to reaction of the complex with chlorine, 1,2-dichloropropane was also formed.

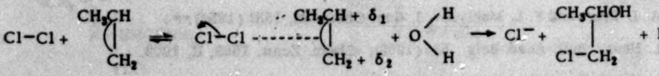
As a result, it was established that a mixture of halogen and propylene under suitable conditions can serve as a β-haloisopropylating agent. In accord with this the reaction of chlorine with propylene in molten benzenesulfonic acid leads to the formation of β-chloroisopropyl benzenesulfonate

$$Cl_2 + CH_2{=}CH{-}CH_3 + C_6H_5SO_3H \longrightarrow ClCH_2{-}CH(OSO_2C_6H_5){-}CH_3 + HCl. \qquad (3)$$

This conclusion was confirmed by the ease with which the reaction product decomposed when heated in the presence of acids with the formation of allyl chloride

$$CH_2ClCH(OSO_2C_6H_5){-}CH_3 \xrightarrow{t} CH_2Cl{-}CH{=}CH_2 + C_6H_5SO_3H. \qquad (4)$$

The reaction between halogen and propylene in water proceeds, according to our views, also through the intermediate creation of a complex of Type (1). Here the predominant formation of β-haloisopropyl alcohols



$$Cl{-}Cl + \begin{array}{c} CH_3CH \\ \| \\ CH_2 \end{array} \rightleftharpoons \overset{\frown}{Cl{-}Cl} \dashleftarrow \begin{array}{c} CH_3CH + \delta_1 \\ \| \\ CH_2 + \delta_2 \end{array} + O\begin{array}{l} \diagup H \\ \diagdown H \end{array} \longrightarrow Cl^- + \begin{array}{c} CH_3CHOH \\ | \\ Cl{-}CH_2 \end{array} + H^+ \qquad (5)$$

speaks in favor of our interpretation of the reaction mechanism.

The order of addition in conjugation reactions to other unsymmetrical olefins can be determined in the same manner. Thus, taking into account the favorable influence of the phenyl group in stabilizing the positive charge on the carbon connected to it, it follows that the products of addition to styrene, in accord with the experimental data, will have the structure of type $C_6H_5CHA{-}CH_2Cl$.

As regards the order of addition, in conjugation reactions the halogen atom corresponds to the hydrogen atom in those cases where the addition of hydrogen halide acids is of the ionic type. This analogy can be used for practical purposes. The well-known Markovnikov rule can be used with success here.

EXPERIMENTAL

1. Preparation of β-Chloroisopropyl Acetate. Into a 150 ml reactor was poured 100 g of glacial acetic acid and with vigorous agitation there was simultaneously passed for 2 hours about 15 liters of chlorine and a slightly larger

amount of propylene. The reaction mass was mixed with water and strong sodium hydroxide solution was added to slight alkalinity. After washing with water and drying over calcium chloride the organic layer was fractionally distilled through a dephlegmator. The following fractions were collected: 1st) 95-110°, 17.1 g; 2nd) 110-145°, 5.0 g; 3rd) 145-150°, 21.7 g. Redistillation gave a fraction with b.p. 149-150°, being β -chloroisopropyl acetate [3].

d_4^{20} 1.1012, n_D^{20} 1.4270, MR_D 31.87; calculated 31.83.
Found %: Cl 25.97. $C_5H_9O_2Cl$. Calculated %: C 25.89.

On heating the ester with sodium iodide in acetone solution, and then the iodo derivative with silver nitrate, a product was obtained that gave the characteristic reactions of a primary nitro compound and we failed to reveal the presence of any other possible isomer.

2. Preparation of β -Chloroisopropyl Formate and β -Chloroisopropyl Alcohol. The conjugation reaction of propylene with chlorine in a solution of 92 g of formic acid (d 1.22) was run the same as the just described experiment. Fractional distillation gave the following fractions: 1st) 95-125°, 12.2 g; 2nd) 125-136°, 3.4 g; 3rd) 136-138°, 19.4 g.

The 3rd fraction was the earlier unknown β -chloroisopropyl formate.

B.p. 137°, d_4^{20} 1.1489, n_D^{20} 1.4260, MR_D 27.32; calculated 27.19.
Found %: Cl 28.77. $C_4H_7O_2Cl$. Calculated %: Cl 28.94.

The obtained ester, similar to the acetate, can be converted into the primary nitro compound. When heated with excess 3% hydrogen chloride solution in methyl alcohol it is almost quantitatively converted into methyl formate and β -chloroisopropyl alcohol [4,5].

B.p. 126° (743 mm), d^{20} 1.111, n_D^{20} 1.4390.

3. Preparation of β -Chloroisopropyl Benzenesulfonate. The reaction was run in the same apparatus. Through the melt of 144 g of anhydrous benzenesulfonic acid at 65° there was passed for 2.5 hours about 20 liters of chlorine and a slightly larger amount of propylene. After suitable treatment [2] there was obtained 24.2 g of dichloropropane and 128 g (over 50%) of crude ester. When the distillation of large amounts was attempted the ester readily decomposed with the formation of benzenesulfonic acid in the residue and a mixture of 1-chloropropene with allyl chloride in the distillate; rapid distillation of 20-30 g batches at 3-4 mm was entirely satisfactory and proceeded with hardly any residue at 160-170°.

d_4^{20} 1.3014, n_D^{20} 1.5220, MR_D 54.97; calculated 54.84.
Found %: Cl 14.70. $C_9H_{11}O_3SCl$. Calculated %: Cl 15.12.

SUMMARY

In accord with the theories for conjugation addition reactions it was shown that β -chloroisopropyl formate, the acetate and the benzenesulfonate are formed when chlorine reacts with propylene in the respective acids.

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*Consultants Bureau Translation, p. 1607

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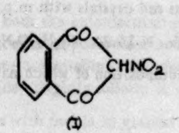
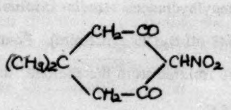
NITRODIMEDON AND SOME OF ITS DERIVATIVES

E. Gudrinietse, O. Neiland and G. Vanag

2-Nitro-1,3-indandione (I) is not only an excellent analytical reagent [1,2], but is also the starting material for the synthesis of a number of new compounds [2-5]; consequently it was of interest in this respect to also study other cyclic β-diketones, nitrated at the active methylene group. A comparatively readily available cyclic β-diketone is dimedon, or 1,1-dimethyl-3,5-cyclohexanedione. Its nitro derivative (II) is already known in the literature and is obtained by the nitration of dimedon with nitrogen oxides. We were able to obtain nitrodimedon in slightly better than 50 % yield by the nitration of dimedon with fuming nitric acid. The compound was obtained as colorless crystals with m.p. 105°; water solutions are colored yellow.

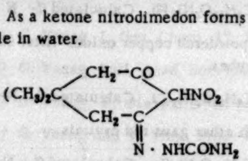

(I)

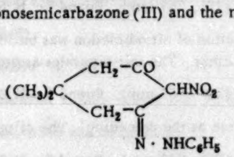

(II)

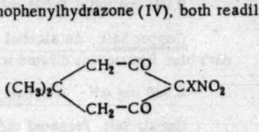
Nitrodimedon, the same as nitroindandione, is a strong acid. It readily forms salts, usually quite soluble in water. Some of the organic salts of nitrodimedon have already been described in the literature [6]. We prepared a number of unknown inorganic salts of nitrodimedon, and also a number of salts with organic bases. The bivalent iron salt, being so characteristic for nitroindandione [7], is also characteristic for nitrodimedon. In contrast to all of the other nitrodimedon salts it is dark purple in color; in water it dissolves with a green color.

The salts of nitrodimedon with organic bases, even with the primary aromatic amines, are soluble in water; this means that nitrodimedon is less suitable than nitroindandione for separating these amines from solutions. The salts of some of the tertiary amines separate as oils, which was also observed for some of the tertiary amine salts of nitroindandione [8].

As a ketone nitrodimedon forms the monosemicarbazone (III) and the monophenylhydrazone (IV), both readily soluble in water.


(III)


(IV)


(X = Cl, Br)

(V)

Similar to nitroindandione, nitrodimedon is readily brominated and chlorinated. The obtained halogenated derivatives (V) in aqueous solutions are decomposed with the cleavage of hypochlorous or hypobromous acid.

It is known that dimedon is a reagent for aldehydes; nitrodimedon with aldehydes fails to give any characteristic reactions.

EXPERIMENTAL

4-Nitro-1,1-dimethyl-3,5-cyclohexanedione (Nitrodimedon) (II)

In a three-necked round-bottomed flask with stirrer (with mercury seal), dropping funnel and reflux condenser was placed 20 g of well crushed dimedon and 80 ml of diethyl ether. The flask was immersed in a cooling mixture (ice and salt) and with vigorous stirring from the dropping funnel was added 12 ml of fuming nitric acid (d 1.5). After this the reaction mass was stirred without cooling until the brown color had disappeared. Then another 3-5 ml of the same nitric acid was added. Violent reaction takes place and the flask has to be cooled (with ice and salt). Usually the flask contents become colorless. The ether is removed in vacuo (water-jet pump) at room temperature. The flask contents crystallize into a hard mass. The crystals are separated and washed with a little ether. Yield of nitrodimedon 14 g (56.3 %). M.p. 102°.

3.229 mg sub.: 0.202 ml N_2 (16°, 772 mm). Found %: N 7.51. $C_8H_{11}O_4N$. Calculated %: N 7.57.

Nitrodimedon can be recrystallized from ether-gasoline mixture. Colorless prisms with m.p. 105°. Nitrodimedon is readily soluble in water, alcohol, benzene, glacial acetic acid and acetone, slightly soluble in ether and carbon tetrachloride, and insoluble in gasoline. Its solutions in water and alcohol (96%) are colored yellow, in the other mentioned solvents colorless.

Only with the free semicarbazide in anhydrous alcohol solution were we able to obtain the nitrodimedon semicarbazone. Yellow crystals. M.p. 240-241°. Difficultly soluble in alcohol and ether, readily soluble in glacial acetic acid and in water.

4.357 mg sub.: 0.902 ml N_2 (23°, 746 mm). Found %: N 23.43. $C_9H_{14}O_4N_4$. Calculated %: N 23.14.

Nitrodimedon Phenylhydrazone. When an alcohol solution of nitrodimedon was boiled with phenylhydrazine two kinds of crystals were obtained (probably mono- and bis-phenylhydrazones). When the mixture is boiled with acetone the nitrodimedon monophenylhydrazone remains insoluble as red crystals with m.p. 222.5°.

2.657 mg sub.: 0.348 ml N_2 (20°, 764 mm). Found %: N 15.34. $C_{14}H_{17}O_3N_3$. Calculated %: N 15.27.

Yellow crystals were isolated from the acetone, the composition of which has not yet been determined.

Nitrodimedon Salts

Sodium Salt. An alcohol solution of nitrodimedon was boiled with sodium carbonate and filtered. The filtrate was diluted with ether. The sodium salt of nitrodimedon separated as yellow plates.

3.186 mg sub.: 0.165 ml N_2 (19°, 781 mm). Found %: N 6.22. $C_8H_{10}O_4NNa$. Calculated %: N 6.22.

Silver Salt. Prepared by the reaction of nitrodimedon with silver oxide in alcohol solution. When compared with other nitrodimedon salts it is less soluble in alcohol and on cooling its solution it separates as yellow glistening crystals.

3.857 mg sub.: 0.150 ml N_2 (15°, 764 mm). 0.1062 g sub.: 0.0519 g AgCl. Found %: N 4.63; Ag 36.71. $C_8H_{10}O_4NAg$. Calculated %: N 4.79; Ag 36.98.

Lead Salt. Prepared from nitrodimedon and lead oxide (in alcohol solution). Yellow plates.

2.271 mg sub.: 0.091 ml N_2 (19°, 757 mm). Found %: N 5.02 $(C_8H_{10}O_4N)_2Pb$. Calculated %: N 4.87.

Copper Salt. An alcohol solution of nitrodimedon was boiled with powdered copper oxide. After filtration the dark blue filtrate was diluted with ether. The salt separates as greenish cubes.

2.586 mg sub.: 0.137 ml N_2 (19°, 756 mm). Found %: N 6.16. $(C_8H_{10}O_4N)_2Cu$. Calculated %: N 6.49.

Cobalt Salt. Prepared the same as the preceding. The dilution with ether gave red crystals.

3.686 mg sub.: 0.192 ml N_2 (22°, 766 mm). Found %: N 6.07. $(C_8H_{10}O_4N)_2Co$. Calculated %: N 6.56.

Bivalent Iron Salt (Ferrous Salt). Prepared by boiling iron sulfide (FeS) with an alcohol solution of nitrodimedon. Forms dark purple crystals, dissolving in water with a dark-green color.

2.986 mg sub.: 0.174 ml N_2 (18°, 762 mm). Found %: N 6.85. $(C_8H_{10}O_4N)_2Fe$. Calculated %: N 6.60.

When heated the nitrodimedon salts fail to melt and instead decompose violently (with flashing). The least stable is the nitrodimedon silver salt.

Aniline Salt. When an ether solution of aniline is added to an alcohol solution of nitrodimedon the aniline salt of nitrodimedon is obtained as colorless needle crystals. M.p. 151°. Readily soluble in water.

3.786 mg sub.: 0.328 ml N_2 (19°, 772 mm). Found %: N 10.13. $C_{14}H_{18}O_4N_2$. Calculated %: N 10.07.

p-Toluidine Salt. Prepared the same as the aniline salt. Colorless crystals. M.p. 160°.

3.829 mg sub.: 0.326 ml N_2 (22°, 755 mm). Found %: N 9.79. $C_{15}H_{20}O_4N_2$. Calculated %: N 9.57.

β-Naphthylamine Salt. Prepared the same as the aniline salt. Colorless crystals. M.p. 153°.

3.843 mg sub.: 0.289 ml N_2 (23°, 757 mm). Found %: N 8.63. $C_{18}H_{20}O_4N_2$. Calculated %: N 8.54.

4-Nitro-4-chloro-1,1-dimethyl-3-5-cyclohexanedione (Chloronitrodimedon) (V; X = Cl)

A solution of 1.5 g of nitrodimedon in 50 ml of water was treated with chlorine. A white precipitate separated. Filtered and washed with water. Yield nearly quantitative. Recrystallized from carbon tetrachloride. Colorless crystals. M.p. 121°.

2.200 mg sub.: 0.123 ml N_2 (23°, 766 mm). 5.057 mg sub.: 3.257 mg AgCl. Found %: N 6.50; Cl 15.93. $C_8H_{10}O_4NCl$. Calculated %: N 6.38; Cl 16.17.

4-Nitro-4-bromo-1,1-dimethyl-3,5-cyclohexanedione (Bromonitrodimedon) (V; X = Br)

Obtained the same as the preceding from the dimedon and bromine water. Colorless crystals with m.p. 141°.

3.814 mg sub.: 0.166 ml N_2 (22°, 757 mm). 3.000 mg sub.: 2.114 mg AgBr. Found %: N 5.02; Br 29.98. $C_8H_{10}O_4NBr$. Calculated %: N 5.30; Br 30.30.

When heated with water both the chloronitrodimedon and the bromonitrodimedon revert back to nitrodimedon with the cleavage of hypochlorous or hypobromous acid. Both liberate iodine from potassium iodide solution. Both the chloro- and bromonitrodimedons are soluble in alcohol, benzene and carbon tetrachloride; slightly soluble in alcohol, benzene and carbon tetrachloride; slightly solbule in ether, and insoluble in water.

Bromonitrodimedon gives with indole in glacial acetic acid a brown color, at higher indole concentrations a brown precipitate separates.

SUMMARY

1. A method was developed for obtaining nitrodimedon by the nitration of dimedon with fuming nitric acid.

2. Some of the salts of nitrodimedon with inorganic and organic bases, readily soluble in water and in alcohol, were described.

3. The bromo- and chloro- derivatives of nitrodimedon were obtained.

4. The mono-semicarbazone and mono-phenylhydrazone of nitrodimedon were prepared.

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* Consulants Bureau Translation, p 1543.

** Consultants Bureau Translation, p 1551.

p-Nitroanilinium salt. Prepared the same as the [illegible] salt; [illegible] crystals. [illegible]

[illegible] mg sub.: [illegible] ml N_2 ([illegible]°, [illegible] mm). Found %: N [illegible]. [illegible]. Calculated %: N [illegible].

5-Nitro-4-chloro-1,1-dimethyl-3,4-cyclohexanedione (Chloronitrodimedone) (V, X = Cl)

A solution of 1.5 g of nitrodimedone in 25 ml of water was treated with chlorine. A white precipitate separated, was filtered and washed with water. Yield nearly quantitative. [illegible] crystals, M.p. 124°.

[illegible] mg sub.: [illegible] ml N_2 ([illegible]°, [illegible] mm). [illegible] mg sub.: [illegible] mg AgCl. Found %: N [illegible], Cl [illegible]. $C_8H_{10}O_4NCl$. Calculated %: N [illegible], Cl [illegible].

5-Nitro-4-bromo-1,1-dimethyl-3,4-cyclohexanedione (Bromonitrodimedone) (V, X = Br)

Obtained the same as the preceding, using the [illegible]. [illegible] crystals with m.p. [illegible]°.

[illegible] mg sub.: [illegible] ml N_2 ([illegible]°, [illegible] mm). [illegible] mg sub.: [illegible] mg AgBr. Found %: N [illegible], Br [illegible]. $C_8H_{10}O_4NBr$. Calculated %: N [illegible], Br [illegible].

When heated with water both the chloronitrodimedone and the bromonitrodimedone revert back to nitrodimedone with the cleavage of hypochlorous or hypobromous acid. Both [illegible]. Both the chloro- and bromonitrodimedones are soluble in alcohol, benzene and carbon tetrachloride, slightly soluble in ether, and insoluble in water.

Bromonitrodimedone gives with aniline in glacial acetic acid a brown color; at higher [illegible] concentrations a brown precipitate separates.

SUMMARY

1. A method was developed for obtaining nitrodimedone by the nitration of dimedone with fuming nitric acid.

2. Salts of [illegible] of nitrodimedone with [illegible] and organic bases, readily soluble in water and in alcohol, were described.

3. The bromo- and chloro- derivatives of nitrodimedone were obtained.

4. The [illegible] and [illegible] were suggested.

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* Consultants Bureau Translation, p. [illegible].

** Consultants Bureau Translation, p. [illegible].

PREPARATION OF 4(or 5)-IMIDAZOLYLMETHYL ESTERS OF 4-AMINO AND 4-BUTYLAMINOBENZOIC ACIDS

O. K. Nikiforova

In connection with the ever increasing needs of native medicine for histamine, used in the therapy of various ailments, the Western Siberian Affiliate of the Academy of Sciences of the USSR undertook the task of synthesizing histamine by a new method.

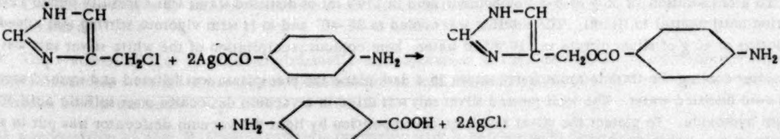
In contrast to the existing methods for the preparation of this compound, in the present case readily available invert sugar [1] was used as the crude for the synthesis. This method also makes it possible to obtain in the pure form and in any amount the earlier difficultly available intermediates: 4(or 5)-(hydroxymethyl) imidazole and 4(or 5)-(chloromethyl) imidazole.

As is known, the physiological activity of histamine for the most part depends on its imidazole grouping. Imidazole, as well as its simpler derivatives – 4(or 5)-methyl-imidazole, 4(or 5)-(hydroxymethyl) imidazole, 4(or 5)-(chloromethyl)-imidazole and others – produce to different degrees contraction in the isolated uterus and intestine, stimulate peristalsis and reduce blood pressure [7]. The coupling of the imidazole nucleus with the ethylamine radical explains the specific pain-killing action of histamine. The condensation of imidazole derivatives and 4-aminobenzoic acid with the formation of the ester grouping characteristic for compounds of the type of novocaine promised to give substances that could qualify as new local anesthetics.

With this in mind the 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid and the 4(or 5)-imidazolylmethyl ester of 4-butylaminobenzoic acid were synthesized, the methods for the preparation of which is the subject of the present paper.

As starting products, containing the imidazole grouping, were used the intermediates in the synthesis of histamine, namely 4(or 5)-(hydroxymethyl) imidazole and 4(or 5)-(chloromethyl) imidazole. 4(or 5)-(Hydroxymethyl) imidazole was synthesized by the method of Kulev and Onishchuk [1]. 4(or 5)-(Chloromethyl) imidazole was obtained by the action of thionyl chloride on 4(or 5)-(hydroxymethyl)-imidazole [2].

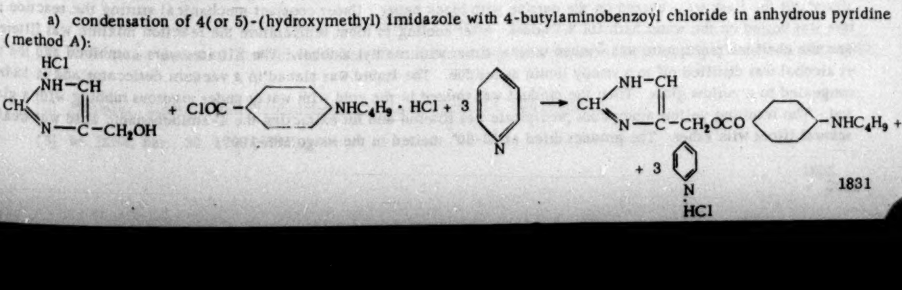
The condensation of 4(or 5)-(chloromethyl) imidazole with the silver salt of 4-aminobenzoic acid in anhydrous methyl alcohol gave the 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid:



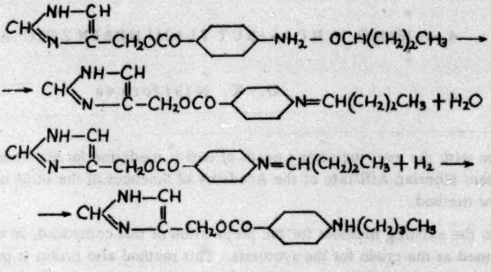
The silver salt of aminobenzoic acid was obtained in the same manner as the silver salt of 4-methylaminobenzoic acid [3].

We were unable to obtain the 4(or 5)-imidazolylmethyl ester of 4-butylaminobenzoic acid through the silver salt of 4-butylaminobenzoic acid. Instead it was obtained by two other methods:

a) condensation of 4(or 5)-(hydroxymethyl) imidazole with 4-butylaminobenzoyl chloride in anhydrous pyridine (method A):



b) butylation of the earlier obtained 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid with butyraldehyde under simultaneous reduction of the azomethine formed in the butylation (method B):



The studies of Shapiro [4], Clinton [5] and others were used in developing the second method, which studies indicated the possibility of butylating certain esters of 4-aminobenzoic acid with butyraldehyde.

4-Butylaminobenzoic acid and the hydrochloride of butylaminobenzoyl chloride were synthesized by known methods [6].

The pharmacological studies, made at the Pharmacology Cathedra of the New Siberian Medical Institute, revealed that the obtained esters possess local anesthetic properties.

EXPERIMENTAL

1. 4(or 5)-(Chloromethyl)imidazole Hydrochloride

To 50 g of 4(or 5)-(hydroxymethyl) imidazole hydrochloride was added in the cold 86 ml of thionyl chloride. The flask was quickly connected to a bulb condenser, fitted with a calcium chloride tube. Vigorous reaction in the cold proceeded for 10 minutes, after which the evolution of gases almost ceased. The reaction mass was heated on the water bath at 80-85° for 40 minutes, and then the excess thionyl chloride was vacuum distilled. After the distillation there remained in the flask a yellow deposit of 4(or 5)-(chloromethyl) imidazole. The crude product was recrystallized from anhydrous ethyl alcohol under boiling with animal charcoal. Purification gave 43.6 g of 4(or 5)-(chloromethyl) imidazole hydrochloride with m.p. 139-140° (literature: 140-141°). Yield of pure product 77 %.

2. Silver Salt of 4-Aminobenzoic Acid

To a hot solution of 35 g of 4-aminobenzoic acid in 1700 ml of distilled water was carefully added 12% ammonia solution until neutral to litmus. The solution was cooled to 35-40° and to it with vigorous stirring was added in portions a solution of 40 g of silver nitrate in 110 ml of water; here copious precipitation of the white silver salt was observed.

After cooling the flask to room temperature in a dark place the precipitate was filtered and washed several times with cold distilled water. The well pressed silver salt was dried in a vacuum desiccator over sulfuric acid or solid potassium hydroxide. To protect the silver salt from decomposition by light the vacuum desiccator was put in a dark place. Weight of dry silver salt of 4-aminobenzoic acid 49 g. Yield 79%.

3. 4(or 5)-Imidazolylmethyl Ester of 4-Aminobenzoic Acid

In a flask, fitted with a mercury seal stirrer, was placed 49 g of silver 4-aminobenzoate, 15.4 g of 4(or 5)-(chloromethyl)-imidazole and 250 ml of anhydrous methyl alcohol. For avoiding the action of light and decomposition of the silver salt the flask was covered on the outside with black paper. Under constant mechanical stirring the reaction mixture was boiled on the water bath for 3.5 hours. After cooling to room temperature the reaction mixture was filtered and the obtained precipitate was washed several times with methyl alcohol. The filtrates were combined and the methyl alcohol was distilled off to a sirupy liquid as residue. The liquid was placed in a vacuum desiccator and in 12 hours congealed to a yellow glass. Then the product was treated in the cold with water under vigorous rubbing with a glass rod. The resulting yellow amorphous precipitate was filtered and for extracting the 4-aminobenzoic acid was treated several times with ether. The product dried at 50-60° melted in the range 186-190°.

Several recrystallizations from 50% ethyl alcohol gave 10.7 g of pure compound with m.p. 216°. Yield 49.1%.

The 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid crystallizes as glistening white leaflets, insoluble in ether, difficultly soluble in cold water, moderately soluble in hot water, and readily soluble in ethyl and methyl alcohols.

When coupled with diazotized sulfanilic acid it gives a brownish-red color, characteristic for imidazole derivatives.

6.151, 6.502 mg sub.: 13.670, 14.469 mg CO_2; 2.869, 3.016 mg H_2O. Found %: C 60.65, 60.73; H 5.22, 5.19. $C_{11}H_{11}O_2N_3$. Calculated %: C 60.81; H 5.10.

4. 4(or 5)-Imidazolylmethyl Ester of 4-Butylaminobenzoic Acid

Method A. In a two-necked round bottomed flask, fitted with mercury seal and mechanical stirrer, was placed 90 ml of dry, freshly distilled pyridine and 8.2 g of 4(or 5)-(hydroxymethyl)-imidazole hydrochloride. The solution of the (hydroxymethyl) imidazole in the pyridine began at room temperature and was completed on heating the mixture to 30-40° on the water bath. To the thus obtained homogeneous solution was added in small portions 13 g of 4-butylaminobenzoyl chloride hydrochloride. Then the light brown solution was heated on the water bath with constant stirring for 6 hours. The temperature of the water bath was kept at 60-65° in the early hours, and at 95-100° toward the end. After cooling to room temperature the reaction mixture was poured into cooled 20% sulfuric acid solution. The obtained spongy precipitate was filtered, well washed with 20% soda solution, and then with water. Weight of precipitate 8.2 g. Melting point of the crude product 209-214°.

After several recrystallizations from ethyl alcohol the product melted at 234-234.5°. Weight of purified product 6.0 g. Yield 41%. 4(or 5)-Imidazolylmethyl 4-butylaminobenzoate is practically insoluble in cold water, difficultly soluble in hot water, and readily soluble in ethyl alcohol, alcohol-water mixture, benzene, pyridine and glacial acetic acid.

Method B. A mixture of 3.5 g of 4(or 5)-imidazolymethyl 4-aminobenzoate and 3 ml of butyraldehyde was heated on the water bath for 1 hour. Then 15 ml of alcohol was added to the reaction mass, after which it was heated another 40 minutes. The reaction mixture was let stand 12-14 hours, after which 15 ml of glacial acetic acid and 5 g of zinc dust were added. The reduction was run for 3 hours with boiling on the water bath and mechanical stirring. At the end of reaction the mixture was filtered and the filtrate was poured into 100 ml of water and ice. The liquid was made alkaline to litmus with sodium carbonate solution, the precipitate was filtered, washed with cold water, and dried.

After recrystallization from alcohol the ester melted at 234°. Yield 2 g (46%).

6.985, 7.895 mg sub.: 16.855, 19.039 mg CO_2; 4.363, 4.974 mg H_2O. Found %: C 65.85, 65.81; H 6.99, 7.05. $C_{15}H_{19}O_2N_3$. Calculated %: C 65.91; H 7.01.

SUMMARY

1. The unknown 4(or 5)-imidazolylmethyl 4-aminobenzoate and 4(or 5)-imidazolylmethyl 4-butylaminobenzoate were synthesized.

2. The synthesis of 4(or 5)-imidazolylmethyl 4-aminobenzoate was realized by the condensation of 4(or 5)-(chloromethyl) imidazole with the silver salt of 4-aminobenzoic acid. 4(or 5)-imidazolylmethyl 4-butylaminobenzoate was obtained by two methods:

a) condensation of 4(or 5)-(hydroxymethyl) imidazole with 4-butylaminobenzoyl chloride;

b) butylation of 4(or 5)-imidazolylmethyl 4-aminobenzoate with butyraldehyde and reduction of the resulting azomethine.

3. The obtained esters possess local anesthetic properties.

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Laboratory of Organic Synthesis of the Western Siberian Affiliate of the Academy of Sciences of the USSR

INVESTIGATION OF ORGANIC ISOCYANATES

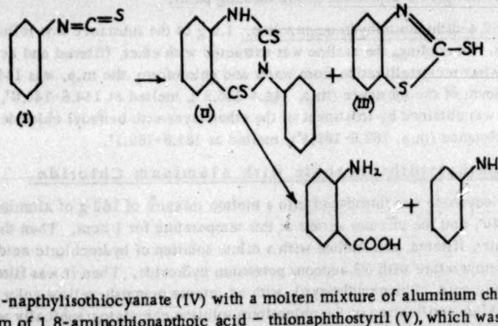
IV. TRANSFORMATION OF PHENYL- AND 1-NAPTHYLISOTHIOCYANATES BY TREATMENT WITH ALUMINUM CHLORIDE

N. S. Dokunikhin and L. A. Gaeva

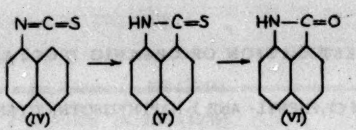
It was shown earlier that, by reaction with molten mixtures of aluminum chloride and sodium chloride, phenylisocyanate yields 3-phenyl-2,4-dioxotetrahydroquinazoline [1], but 1-naphthylisocyanate isomerizes to the lactam of 1,8-aminonaphthoic acid – napthostyril [2]. It is of interest to study the transformation of the corresponding isothiocyanates under similar conditions.

It is known that, with the aromatic hydrocarbons [3], and especially with the phenolic esters [4], in the presence of aluminum chloride, the organic isothiocyanates form substituted amides of thiocarboxylic acids, which are analogous to the substituted amides of carboxylic acids obtained from the isocyanates, according to Leuckart [5]. Observing the reaction of the phenyl derivative of mustard oil with benzene and aluminum chloride, Friedmann and Gattermann [3] isolated thiobenzanilide and a product that had a m.p. of 154°, was insoluble in alkali, contained one atom of sulfur to two molecules of phenylisothiocyanate, $(C_6H_5NCS)_2S$, and at the same time had an odor indicating the presence of phenylisonitrile. The authors showed the identity of the isolated substance with the compound that Proskauer and Sell [6] obtained by reaction of bromine and the phenyl derivative of mustard oil, followed by treatment with alcohol. Friedmann and Gattermann obtained the same substance without the use of benzene, by warming a mixture of the pehnyl derivative of mustard oil and aluminum chloride for a period of 15 minutes on the water bath. The reaction of phenylisothiocyanate with aluminum chloride at higher temperatures was not described. From the products of the reaction of phenylisothiocyanate (I) with a molten mixture of aluminum chloride and sodium chloride, we isolated two substances that were soluble in aqueous alkali, and which could be separated by their different degrees of acidity as well as by chromatography.

One of them was identified as 2-mercaptobenzothiazole (III), and the other proved to be 3-phenyl-2,4-dithiontetrahydroquinazoline (II). The structure of the latter was verified by analysis, by determination of the molecular weight, and by cleavage, using hot aqueous alkali, resulting in the formation of aniline and anthranilic acid.



By reaction of 1-napthylisothiocyanate (IV) with a molten mixture of aluminum chloride and sodium chloride, we obtained the lactam of 1,8-aminothionapthoic acid – thionaphthostyril (V), which was soluble in aqueous solutions of alkali at ordinary temperatures, and from which, on acidification, it was precipitated unchanged. By boiling with a 50% solution of potassium hydroxide, followed by heating with hydrochloric acid, the thionaphthostyril (V) was transformed to naphthostyril (VI):



When our work was already completed, a report of an American Patent of 1953 [7] appeared, concerning a method of obtaining naphthostyril by reacting 1-naphthylisocyanate with aluminum chloride. This method differed from that which we described in 1951 [2] for carrying out the reaction with the use of organic solvents, particularly dichlorobenzene. In the text of the reference, the feasibility of obtaining naphthostyril (VI) from 1-naphthylisothiocyanate (IV) was indicated; however, no mention was made of the formation of the thioanalog of naphthostyril (V). Apparently, the latter circumstance is explained by the conditions of treatment of the reaction mass employed by the American investigators (heating with an aqueous solution of alkali, followed by acidification), which as described above, leads to the transformation of thionaphthostyril to napthostyril. Similar treatment of the products of the reaction of 1-napthylisothiocyanate with aluminum chloride, conducted under conditions that we selected, also led directly to napthostyril.

EXPERIMENTAL

1. Reaction of Phenylisothiocyanate with Aluminum Chloride

Into a molten mixture of 160 g of aluminum chloride and 38 g of sodium chloride at 165°, 20 g of phenylisothiocyanate (I) was introduced, and the mixture was stirred for 1 hour at 165-170°. The reaction mixture was then poured into a mixture of ice and water, filtered, and the precipitate was transferred to a dilute solution of hydrochloric acid, and the phenylisothiocyanate not entering into the reaction was removed by steam-distillation. The residue, after distillation, was filtered and the precipitate was stirred with a 5% solution of potassium hydroxide. From the alkaline filtrate, a current of carbon dioxide precipitated at first (pH ≃ 9) 3-phenyl-2,4-dithiontetrahydroquinazoline (II), then precipitated a mixture of the latter with 2-mercaptobenzothiazole (III). The total weight of the products isolated from the alkaline solution was 5.17 g, for compound (II) – 2.04 g, and for compound (III) – 1.73 g.

For 3-pehnyl-2,4-dithiontetrahydroquinazoline (II) – the light yellow, tapering crystals from benzene had a m.p. of 280-294° (with decomposition). They were highly soluble in benzene, chloroform and alcohol.

Found %: C 62.55, 62.37; H 3.94, 3.81; S 22.76, 23.07; N 10.23. 10.03. M (in camphor). 272, 282. $C_{14}H_{10}N_2S_2$.
Calculated %: C 62.22; H 3.70; S 23.70; N 10.37. M 270.

The 2-mercaptobenzothiazole (III), after recrystallization from alcohol, had a m.p. of 173-178°. With a sample of the known substance, it did not give a depression of the melting point.

Cleavage of 3-phenyl-2,4-dithiontetrahydroquinazoline. 1.2 g of the substance was refluxed with 12 ml of 25% aqueous potassium hydroxide. On cooling, the aniline was extracted with ether, filtered and acidified. We obtained 0.43 g of anthranilic acid. After recrystallization from water and chloroform, the m.p. was 144.2-145.2°. The mixture, containing a known amount of the substance (m.p. 144.4-145.2°), melted at 144.6-145.6°. 0.37 g of benzanilide with a m.p. of 161.2-162.1° was obtained by treatment of the ether layer with benzoyl chloride and aqueous alkali. A mixture with the known substance (m.p. 162.6-163.4°), melted at 161.8-163.1°.

2. Reaction of 1-Naphthylisothiocyanate with Aluminum Chloride

20 g of 1-napthylisothiocyanate was introduced into a molten mixture of 160 g of aluminum chloride and 38 g of sodium chloride at 165-170°, and the mixture stirred at this temperature for 1 hour. Then the substance was poured into a mixture of ice and water, filtered, and washed with a dilute solution of hydrochloric acid and water. The residue was stirred at room temperature with 5% aqueous potassium hydroxide. Then it was filtered, and the filtrate was acidified with hydrochloric acid. Thionaphthostyril, with an intense orangish-yellow color, was precipitated. The yield was 5.2 g (26%). After purification of the chloroform solution chromatographically with aluminum oxide, and after crystallization from benzene, the m.p. was 156.6-157.6°. The precipitate consisted of yellow needles. They were highly soluble in benzene and chloroform, but insoluble in water.

Found %: C 71.27, 71.55; H 3.83, 3.82; S 16.87, 17.47; N 6.78, 6.97. M (in camphor) 175, 191. $C_{11}H_7NS$.
Calculated %: C 71.35; H 3.78; S 17.29; N 7.56. M 185.

Transformation of thionapthostyril to naphthostyril. 0.35 g of the substance was boiled for a period of 12 hours in 30 ml of 50% solution of potassium hydroxide, the mixture then diluted with 60 ml of water, filtered, hydrochloric acid added to the filtrate until the pH was 9, and the filtrate finally poured into a mixture of ice and hydrochloric acid. It was heated to boiling and filtered. On cooling the filtrate, light yellow flakes of naphthostyril precipitated. The yield was 0.24 g (75.23%), and the m.p. was 180.2-181.2°; a mixture with the known substance (m.p. 180.0-181.2°), melted at 180.0-181.2°.

SUMMARY

1. The reaction of phenylisothiocyanate with aluminum chloride yielded 3-phenyl-2,4-dithiontetrahydroquinazoline and 2-mercaptobenzothiazole.

2. The reaction of 1-napthylisothiocyanate with aluminum chloride yielded the lactam of 1,8-aminothionapthoic acid – thionaphthostyril, was obtained.

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* See Consultants Bureau English translation, page 629.

** See Consultants Bureau English translation, page 835.

Transformation of thiocarbamyl to [illegible]. 0.90 g of the substance was boiled for a period of 12 hours in 30 ml of 25% solution of potassium hydroxide, the mixture then diluted with 60 ml of water, filtered, hydrochloric acid added to the filtrate until the pH was 6, and the filtrate finally poured into a mixture of ice and hydrochloric acid. It was heated to boiling and filtered. On cooling the filtrate, light yellow flakes of [illegible] precipitated. The yield was 0.28 g (75.58%), and the m.p. was 180.5-181.5°; a mixture with the known substance (m.p. [illegible]) melted at 180.0-181.0°.

SUMMARY

1. The reaction of phenylhydrazones with aluminum chloride yielded [illegible] and 2 [illegible].

2. The reaction of [illegible] with aluminum chloride yielded [illegible] and [illegible], was obtained.

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(2) N. S. Dokunikhin, L. A. Gaeva, I. D. [illegible], Dokl. Akad. Nauk SSSR 81, 1073 (1951); N. S. Dokunikhin, I. D. [illegible], J. Gen. Chem. 25, 798 (1955).**

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* See Consultants Bureau English translation, page 873.

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SYNTHESIS OF 1,1-PENTAMETHYLENEGLYCEROL

A. Ya. Berlin and L. V. Sokolova

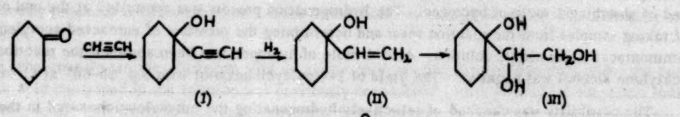
Only Azerbaev [1] has described 1,1-pentamethyleneglycerol [1-(1-hydroxycyclohexyl)-1,2-ethanediol] in the literature, having obtained it by the oxidation of 1-vinylcyclohexanol with potassium permanganate. However, the data given in this paper are extremely limited and do not permit judging the possibility of using the given method for preparing enough of the material in which we were interested.

Proceeding from cyclohexanone we outlined two methods for the synthesis of 1,1-pentamethyleneglycerol (III):

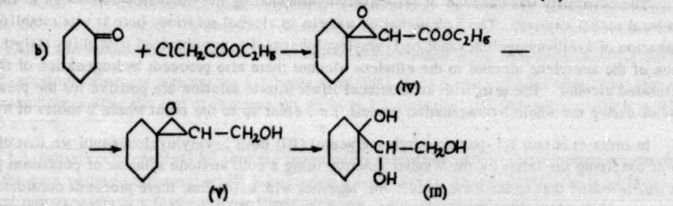
a) via 1-ethynylcyclohexanol (I) and 1-vinylcyclohexanol (II) with subsequent oxidation of the latter, and

b) via the ester of β,β-pentamethyleneglycidic acid (IV) and 3,3-pentamethyleneglycidol (V).

a)



b)

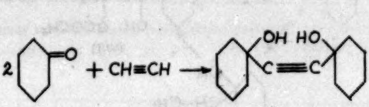


The performed experiments revealed that under definite conditions both of these schemes are practical.

A. Preparation of 1,1-Pentamethyleneglycerol via 1-Vinylcyclohexanol

Using the Favorsky method [2] we obtained 1-ethynylcyclohexanol (I) by the treatment of cyclohexanone with acetylene in ether in the presence of powdered potassium hydroxide. To obtain a good yield of the reaction product it is necessary to observe certain conditions.

First it is necessary to pass acetylene into the mixture of anhydrous ether and powdered potassium hydroxide for approximately an hour before beginning to add the cyclohexanone. Such saturation of the reaction medium with acetylene assures its presence in excess at the start of the reaction, which prevents the possibility of one mole of acetylene condensing with two moles of cyclohexanone to yield the compound bis(hydroxycyclohexyl)acetylene.



From this it follows that during the reaction process the cyclohexanone should be added quite slowly to the mixture of ether and powdered potassium hydroxide with constant passage of acetylene. After all of the cyclohexanone has been added it is recommended that the passage of acetylene be continued for some time until absorption ceases.

The potassium hydroxide used as condensing agent should be freshly ground, otherwise the carbonate film formed on its surface hinders reaction.

Constant vigorous stirring of the reaction mass is necessary, since it gradually thickens considerably in measure with reaction.

It is necessary to work up the reaction mixture the same day, immediately after termination of acetylene passage, since it was repeatedly noticed that if the reaction mass stood after the conclusion of ketone addition and acetylene passage (or was not kept sufficiently cool), then the yield of the acetylene alcohol was reduced and the yield of the corresponding glycol was increased. It is possible that this fact is explained by the reversible nature of the Favorsky reaction [3,4].

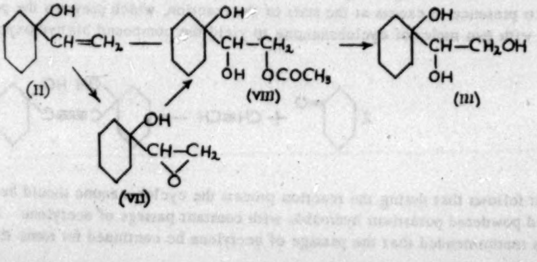
The yield of ethynylcyclohexanol with b.p. 62.5-63° at 8 mm and m.p. 31-32° was 89.5%. The total amount of by-product was only about 5% of the acetylene glycol – bis(1-hydroxycyclohexyl)-acetylene with m.p. 108.5-109°.

The method described by Nazarov and coworkers [5] was used for the selective hydrogenation of 1-ethynylcyclohexanol to 1-vinylcyclohexanol (II), consisting in the use of $Pd-CaCO_3$ as catalyst and termination of the hydrogenation process after one mole of hydrogen had been absorbed. The hydrogenation was run in anhydrous alcohol. As a result of the performed experiments it was revealed that the amount of catalyst, used by Nazarov and coworkers in analogous reactions, could be greatly reduced if the use of the catalyst was repeated several times without interruption (in the present case up to 6 times), adding to it only small amounts of fresh catalyst before each use. The hydrogenation of 1-ethynylcyclohexanol proceeds rapidly and quite smoothly without noticeable retardation of the reaction rate toward the end of absorbing 1 mole of hydrogen. The hydrogenation process was controlled at the end of reaction by the method of taking samples from the reaction mass and determining the presence of unreacted acetylene alcohol with the aid of ammoniacal silver nitrate solution. After 1 mole of hydrogen had been absorbed the reaction for the presence of the acetylene alcohol was negative. The yield of 1-vinylcyclohexanol with b.p. 65-66° at 11 mm was 84.8-85%.

The possibility was checked of selectively hydrogenating the ethynylcyclohexanol in the presence of spent skeletal nickel catalyst. The hydrogenation was run in alcohol solution; here it was established that selective hydrogenation of 1-ethynylcyclohexanol to 1-vinylcyclohexanol is not obtained with this catalyst; together with hydrogenation of the acetylene alcohol to the ethylene alcohol there also proceeds hydrogenation of the ethylene alcohol to the saturated alcohol. The tests with ammoniacal silver nitrate solution are positive for the presence of the acetylene alcohol during the whole hydrogenation process, i.e., clear up to the point where 2 moles of hydrogen are absorbed.

In order to obtain 1,1-pentamethyleneglycerol (III) from 1-vinylcyclohexanol we first of all checked the possibility of oxidizing the latter by the Wagner reaction using a cold acetone solution of potassium permanagnate. However, it was revealed that under these conditions, together with oxidation, there proceeds considerable tarring, preventing the isolation of the desired product. We were able to isolate only a small amount of 1,1-pentamethyleneglycerol, which after repeated recrystallization from ethyl acetate melted at 113-114°. The yield of substance was exceedingly small; consequently we came to reject this method and turned to the attempted oxidation of 1-vinylcyclohexanol with peracetic acid. The oxidation of 1-vinylcyclohexanol with peracids has not been reported before.

It is known that in the oxidation of olefins with an acetic acid solution of peracetic acid it is possible, depending on the reaction conditions, to isolate either the α-oxide, or the monoacetyl derivative of the glycol [6]. In the present case the possible transformations occurring in the oxidation of 1-vinylcyclohexanol and subsequent saponification of the reaction product can be depicted by the following scheme:



As a result, the intermediate products with this scheme should be the oxide of 1-vinylcyclohexanol (1,1-pentamethyleneglycidol) (VII) and the monoacetate of 1,1-pentamethyleneglycerol (VIII).

A solution of peracetic acid in glacial acetic acid was previously prepared from 27% hydrogen peroxide and acetic anhydride in the presence of concentrated sulfuric acid as catalyst [7]. This method is preferable to the method of obtaining peracetic acid without the use of catalyst, since when sulfuric acid is used the amount of extremely explosive diacetyl peroxide formed is usually exceedingly small.

The obtained acetic acid solution of peracetic acid was analyzed for the amount of hydrogen peroxide and peracetic acid. An extremely convenient and simple analysis method consists in the successive titration of the solution aliquot first with hydrogen peroxide and then with peracetic acid [8]. The possibility of titrating hydrogen peroxide in the presence of peracetic acid is conditioned by the fact that hydrogen peroxide is decomposed by permanganate at 0° and considerable dilution, while peracetic acid under these conditions remains unchanged and can later be determined iodometrically. The yield of peracetic acid was 87-89%.

We examined the oxidation of 1-vinylcyclohexanol with peracetic acid under various conditions. According to the data in the literature, sulfuric acid catalyzes the process of opening the α-oxide ring with acetic acid [7]. This circumstance was of interest to us for the reason that as the result of oxidizing 1-vinylcyclohexanol with the obtained, as indicated above, peracetic acid solution, containing sulfuric acid, it would be possible to immediately obtain the monoacetyl derivative of 1,1-pentamethyleneglycerol (VIII). However, as experiment revealed, under these conditions a complex mixture of products is formed, from which, despite repeated fractional distillation, we were unable to isolate any individual substances. Judging from the determination results for labile hydrogen, in the obtained fractions during reaction there simultaneously proceeds dehydration, which leads in the final end to the formation of a difficultly separated mixture of substances.

For this reason we subsequently ran the oxidation with an acetic acid solution of peracetic acid under the conditions where the sulfuric acid contained in the solution was previously neutralized with a solution of anhydrous sodium acetate in glacial acetic acid. This modification gave extremely favorable results. When the oxidation was run with peracetic acid solution, free of sulfuric acid, we obtained, depending on the experimental conditions, either 1,1-pentamethyleneglycidol (VII) or the monoacetyl derivative of 1,1-pentamethyleneglycerol (VIII) in excellent yields.

The oxidation of 1-vinylcyclohexanol was run for 1-2 hours at 20-25°; here it was revealed that if the reaction product was isolated immediately after the end of reaction the yield of 1,1-pentamethyleneglycidol, with b.p. 90-90.5° at 10 mm, was as high as 70%.

The conversion of 1,1-pentamethyleneglycidol into the monoacetyl derivative of 1,1-pentamethyleneglycerol is almost quantitative if the pure pentamethyleneglycidol is heated in glacial acetic acid at 70-80° for 9-10 hours. 1,1-Pentamethyleneglycerol monoacetate is a fairly viscous liquid with b.p. 126-127° at 2-3 mm.

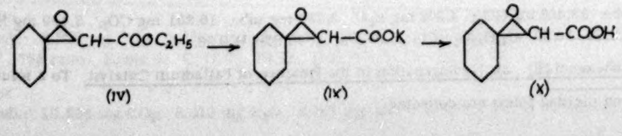
On the basis of the obtained results it can be concluded that it is possible to run the oxidation reaction without isolating the intermediate oxide. Actually, if after adding all of the 1-vinylcyclohexanol to the peracetic acid the whole reaction mixture is heated for 10-11 hours at 70-80°, then the monoacetyl derivative of 1-1-pentamethyleneglycerol is obtained. The yield of acetylated product obtained in this manner was 62-63%.

The monoacetate of 1,1-pentamethyleneglycerol under the influence of alcoholic sodium hydroxide is easily saponified to 1,1-pentamethyleneglycerol (III) with m.p. 113.5-114°.

B. Preparation of 1,1-Pentamethyleneglycerol via 3,3-Pentamethyleneglycidol

The ethyl ester of β,β-pentamethyleneglycidic acid (IV) was easily obtained by the Darzens condensation of cyclohexanone with chloroacetic ester in the presence of sodium ethylate [9].

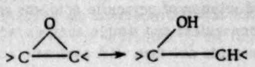
The saponification of the ethyl ester with alcoholic potassium hydroxide gave the difficultly alcohol soluble potassium salt of β,β-pentamethyleneglycidic acid (IX), and from it the unknown free β,β-pentamethyleneglycidic acid (X) as crystals with m.p. 61-62°.



(IV) (IX) (X)

This acid proved to be extremely unstable. Attempts to recrystallize it failed, since here its melting point dropped considerably. After long standing in the air the acid became a tarry mass.

Next it was necessary to reduce the carbethoxy group to the carbinol group ($-COOC_2H_5 \longrightarrow -CH_2OH$), without touching the α -oxide ring. Such catalysts as $LiAlH_4$ are frequently used for reducing the ester linkage to the alcohol. However, up to now this type of reaction has not been tried with glycidic esters. On the contrary, it is known [10] that under the influence of lithium aluminum hydride the α -oxide ring is easily cleaved in accord with the scheme:

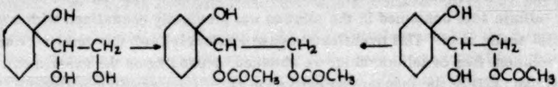


However, by running the reaction at extremely low temperature (−65°) we were able to effect the reduction of the β,β -pentamethyleneglycidic ester with lithium aluminum hydride to the 3,3-pentamethyleneglycidol (V) (b.p. 111-113° at 8 mm) in yields up to 88.5%.

This interesting reaction, showing that under strong cooling the reduction of the ester grouping with lithium aluminum hydride proceeds with much greater ease than does the reductive cleavage of the α -oxide ring, may possibly also prove of value in other similar instances.

The hydrolytic cleavage of the α -oxide ring of 3,3-pentamethyleneglycidol (V) with the formation of 1,1-pentamethyleneglycerol (III) proceeded very smoothly under heating with 2% aqueous acetic acid.

Of the 1,1-pentamethyleneglycerol derivatives prepared the 2,3-diacetate (XI) was obtained by the action of acetic anhydride on the glycerol in pyridine at room temperature.



(III) (XI) (VIII)

The same 1,1-pentamethyleneglycerol 2,3-diacetate is also formed in the acetylation of the monoacetyl derivative of pentamethyleneglycerol (VIII) under the same conditions.

EXPERIMENTAL*

1-Ethynylcyclohexanol (I). In a three-necked flask, fitted with mercury seal stirrer, dropping funnel, tube for acetylene passage and outlet tube, was placed 1600 ml of anhydrous ether and then with stirring was added 210 g of freshly ground powdered dry potassium hydroxide. The mixture cooled to −2 - 0° was saturated with acetylene under stirring for 1-1.5 hours.

To the mixture with vigorous stirring was slowly added 98 g of freshly distilled cyclohexanone over approximately 3 hours, after which the passage of acetylene was continued for some time until absorption ceased. The temperature of the reaction mixture was maintained at −1 - 0° during the whole time of reaction. Then to the reaction mass was added 500-600 ml of water, the ether layer was separated, and the water layer was additionally ether extracted. The combined ether extracts were washed with a saturated sodium bisulfite solution, water, soda solution, again with water, and then dried over anhydous sodium sulfate. After distilling off the ether the substance was vacuum distilled. The yield of 1-ethynylcyclohexanol (b.p. 62.5-63° at 8 mm, m.p. 31-32°, n_D^{20} 1.4786) was 111 g, i.e., 98.5%.

A tarry mass remained in the flask after distillation, from which on addition of a small amount of ether was isolated 5.5 g of the bis(1-hydroxycyclohexyl)acetylene as a white crystalline substance with m.p. 105-107.5°. After recrystallization from petroleum ether, m.p. 108.5-109° (literature m.p. 102-103° [1]). The substance is readily soluble in acetone, alcohol and chloroform, difficultly soluble in benzene, and very difficultly soluble in water.

4.871 mg sub.: 13.400 mg CO_2; 4.302 mg H_2O. 3.730 mg sub.: 10.301 mg CO_2; 3.400 mg H_2O. Found %: C 75.54, 75.36; H 9.94, 10.20. $C_{14}H_{22}O_2$. Calculated %: C 75.63; H 9.98.

1-Vinylcyclohexanol (II). a) Hydrogenation in the Presence of Palladium Catalyst. To a solution of 24 g of

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* All of the given melting points are corrected.

1-ethynylcyclohexanol in 45 ml of anhydrous ethyl alcohol was added 1 g of Pd-$CaCO_3$ (2% Pd) catalyst and the mixture was hydrogenated at room temperature and atmospheric pressure. After the absorption of 1 mole of hydrogen (5150 ml at 21° and 742 mm), for which about 2 hours was required, the hydrogenation was stopped. The catalyst was filtered and the solution was checked for the presence of unreacted acetylene alcohol in the reaction mixture. The test sample failed to give a precipitate with ammoniacal silver nitrate solution. The alcohol was distilled from the solution, while the residue was vacuum distilled. The yield of 1-vinylcyclohexanol was 20.7 g (84.8%), b.p. 65-66° at 11 mm, n_D^{20} 1.4738.

b) Hydrogenation in the Presence of Spent Skeletal Nickel Catalyst. To a solution of 8 g of 1-ethynylcyclohexanol in 30 ml of anhydrous ethyl alcohol was added 0.8 g of spent skeletal nickel catalyst and the mixture was hydrogenated at room temperature and atmospheric pressure. After 1 mole of hydrogen had been absorbed a test sample of the solution gave a voluminous gelatinous white precipitate when treated with ammoniacal silver nitrate solution. The presence of the starting acetylene alcohol continued to be shown even after the absorption of 120, 140, 160 and 180% of hydrogen. After the absorption of 2 moles of hydrogen (336 ml at 20° and 751.5 mm) a test sample of the solution failed to show reaction for the acetylene alcohol.

Oxidation of 1-Vinylcyclohexanol by Wagner. In a three-necked flask, fitted with stirrer, thermometer, dropping funnel and tube descending to the bottom, was placed a 2% solution of 5 g of 1-vinylcyclohexanol in acetone. With vigorous stirring and cooling of the solution to −1-0° there was slowly added dropwise a 2% solution of 5 g of potassium permanganate in acetone, containing the necessary amount of water for the reaction (2 ml). The addition of the permanganate required 8 hours with constant passage of carbon dioxide gas through the reaction mixture.

On conclusion of reaction the passage of carbon dioxide gas was continued for still some time to neutralize the formed alkali. The brown reaction mixture was filtered and the separated manganese dioxide was washed several times with acetone after which the solvent was distilled from the combined acetone solutions; here there remained a heavy dark amorphous mass, from which by treatment with hot ethyl acetate we were able to isolate a small amount of 1,1-pentamethyleneglycerol (III) as a white crystalline substance. After recrystallization from ethyl acetate the 1,1-pentamethyleneglycerol melted at 113-114° (literature [1] 104-105°). The substance is readily soluble in alcohol, acetone and water; soluble in hot ethyl acetate; difficultly soluble in benzene, ether and chloroform.

3.449 mg sub.: 7.592 mg CO_2; 3.091 mg H_2O. 3.979 mg sub.: 8.771 mg CO_2; 3.616 mg H_2O. Found %: C 60.07, 60.15; H 10.03, 10.15. $C_8H_{16}O_3$. Calculated %: C 59.98; H 10.07.

Peracetic Acid. In a three-necked flask, fitted with stirrer, thermometer, reflux condenser and dropping funnel, was placed 25.2 g of 27% hydrogen peroxide. To the well stirred hydrogen peroxide heated to 39-40° was cautiously added dropwise 124.7 g of acetic anhydride, containing 1% of concentrated sulfuric acid. The temperature of the reaction mass was maintained at 39-40° during the whole reaction, both by means of a cooling bath and by regulating the rate of acetic anhydride addition. The addition of the acetic anhydride took 1.5 hours. Based on its analysis [8] the yield of peracetic acid was 13.3 g, i.e., 87.6% based on hydrogen peroxide.

Oxidation of 1-Vinylcyclohexanol with Peracetic Acid in the Presence of Sulfuric Acid. To a solution of 13 g of peracetic acid, obtained as described, with vigorous stirring was added dropwise 18 g of 1-vinylcyclohexanol. The temperature of the reaction mass during reaction was maintained at 20-25°. In measure with vinylcyclohexanol addition the solution first became pink and then turned a brown color. On conclusion of reaction the mixture was analyzed for its peracetic acid content [8]. There was required 2.2 ml of 0.1 N $Na_2S_2O_3$ solution for titrating the iodine liberated by 1 ml of the solution.

The reaction mixture was poured into 10 volumes of water and exhaustively extracted with ether. The ether solution was washed with soda solution, water, and dried over anhydrous sodium sulfate. After removal of the solvent the product was repeatedly fractionally distilled in vacuo, where the following fractions were obtained: 1st) b.p. 43-44° at 12 mm; 2nd) b.p. 68-69.5° at 13 mm; 3rd) 86-87° at 13 mm; 4th) b.p. 102-103° at 13 mm.

1st Fraction:
4.042 mg sub.: 10.862 mg CO_2; 3.291 mg H_2O. 7.780 mg sub.: 0.43 ml CH_4 (15°, 755 mm). Found %: C 73.33; H 9.11; [H^+] 0.18.

2nd Fraction:
3.123 mg sub.: 8.328 mg CO_2; 3.353 mg H_2O. 7.489 mg sub.: 20.009 mg CO_2; 8.891 mg H_2O. 7.61 mg sub.: 1.5 ml CH_4 (17°, 755 mm). Found %: C 72.77, 72.91; H 12.01, 11.95; [H^+] 0.83.

3rd Fraction:
7.062 mg sub.: 18.594 mg CO_2; 6.419 mg H_2O. 3.787 mg sub.: 10.020 mg CO_2; 3.530 mg H_2O. 54.700 mg sub.:

4.89 ml CH_4 (17°, 755 mm). Found %: C 71.85, 72.20; H 10.17, 10.34; $[H^{\circ}]$ 0.37.

4th Fraction:
4.749 mg sub.: 12.428 mg CO_2; 4.359 mg H_2O. 3.032 mg sub.: 7.915 mg CO_2; 2.760 mg H_2O. 11.559 mg sub.: 0.47 ml CH_4 (18°, 755 mm). Found %: C 71.42, 71.24; H 10.27, 10.19; $[H^{\circ}]$ 0.17.

The results of these analyses did not permit us to judge as to the structure of the substances obtained in the given reaction. Only the low labile hydrogen content can be mentioned, which is evidence of partial dehydration.

1,1-Pentamethyleneglycidol (VII). For neutralization of sulfuric acid to the obtained, as indicated above, acetic acid solution of 13 g of peracetic acid was added a 20% solution of potassium acetate in glacial acetic acid until moist Congo paper failed to turn blue. To the well stirred peracetic acid solution was added dropwise over 2 hours 18 g of 1-vinylcyclohexanol. The temperature of the reaction mass during the whole time was maintained at 20-25° with the aid of a cooling bath and by regulating the rate of vinylcyclohexanol addition. The solution remained colorless and clear to the reaction end. Heat evolution was observed for some time after all of the ethylene alcohol had been added.

On conclusion of reaction the mixture was analyzed for its peracetic acid content [8]. The titration of 1 ml of the solution required 2.5 ml of 0.1 N $Na_2S_2O_3$ solution.

The liquid was poured into 10 volumes of water, the solution saturated with sodium sulfate, and then extracted with ethyl acetate. The ethyl acetate extract was washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After removal of ethyl acetate the residual oil was vacuum distilled. Yield of 1,1-pentamethyleneglycidol with b.p. 90-90.5° at 10 mm was 14.2 g (70%). 1,1-Pentamethyleneglycidol is a colorless mobile liquid, readily soluble in the ordinary organic solvents: ether, benzene, acetone, alcohol, xylene, chloroform and ethyl acetate, and difficultly soluble in water.

d_4^{18} 1.0605, n_D^{18} 1.4771, MR_D 37.90; calculated 37.91.
3.685 mg sub.: 9.114 mg CO_2; 3.300 mg H_2O. 15.790 mg sub.: 2.75 ml CH_4 (22°, 757 mm). Found %: C 67.50; H 10.02; $[H^{\circ}]$ 0.72. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.93; $[H^{\circ}]$ 0.71.

1,1-Pentamethyleneglycerol Monoacetate (VIII) From 1,1-Pentamethyleneglycidol. 1,1-Pentamethyleneglycidol (14.2 g) was heated with 7 parts of glacial acetic acid for 9-10 hours at 70-75°. After cooling the reaction mixture was poured into water, the solution was saturated with common salt, and then extracted with ethyl acetate. The ethyl acetate solution was washed with sodium bicarbonate solution, water, and then dried over anhydrous sodium sulfate. Removal of the solvent and vacuum distillation of the residue gave 17.95 g of the 1,1-pentamethyleneglycerol monoacetate with b.p. 126-127° at 2-3 mm. Yield 88.8%. Pentamethyleneglycerol monoacetate is a colorless, viscous, oily liquid, readily soluble in the ordinary organic solvents and difficultly soluble in water.

$d_4^{19.5}$ 1.140, $n_D^{19.5}$ 1.4833, MR_D 50.69; calculated 50.88.
6.213 mg sub.: 13.445 mg CO_2, 4.970 mg H_2O. 3.377 mg sub.: 7.303 mg CO_2; 2.750 mg H_2O. 22.501 mg sub.: 5.2 ml CH_4 (16°, 751 mm). Found %: C 59.06, 59.07; H 8.95, 9.12; $[H^{\circ}]$ 0.97. $C_{10}H_{18}O_4$. Calculated %: C 59.38; H 8.97; $[H^{\circ}]$ 0.99.

1,1-Pentamethyleneglycerol Monoacetate (VIII) From 1-Vinylcyclohexanol. The oxidation of 1-vinylcyclohexanol with peracetic acid solution (after neutralization of the sulfuric acid) was run under the same conditions as described above for the preparation of 1,1-pentamethyleneglycidol. After adding 18.5 g of vinylcyclohexanol to a solution of 13.35 g of peracetic acid the reaction mixture was let stand overnight at room temperature, after which it was heated on the water bath at 70-80° for 10-12 hours. The cooled liquid was poured into water, the solution was saturated with sodium sulfate, and then extracted with ethyl acetate. The separated ethyl acetate solution was washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After solvent removal the substance was distilled at 126-127° and 2-3 mm. The yield of 1,1-pentamethyleneglycerol monoacetate was 18.4 g, or 62.1% based on taken vinylcyclohexanol.

1,1-Pentamethyleneglycerol (III) From the Monoacetate. To 2 g of 1,1-pentamethyleneglycerol monoacetate was added an alcoholic solution of 1.04 g of potassium hydroxide. The saponification was run for 12 hours at room temperature, in which connection the solution gradually turned yellow. After 12 hours the alcohol-alkali solution was acidified with an alcohol solution of hydrochloric acid to weakly acid to Congo, the potassium chloride was filtered and washed with alcohol, after which the alcohol was removed, while the residue was recrystallized from ethyl acetate. The yield of 1,1-pentamethyleneglycerol with m.p. 107.5-108° was 0.79 g, which after 3 recrystallizations from ethyl acetate melted at 113.5-114° and failed to depress the melting point when mixed with the pentamethyleneglycerol that had been obtained by the oxidation of 1-vinylcyclohexanol according to Wagner.

Potassium β,β-Pentamethyleneglycidate (IX). A solution of 6 g of the β,β-pentamethyleneglycidic ester (IV) [9] in anhydrous alcohol was added to an alcohol solution of 3.65 g of potassium hydroxide. Slight heating up of the reaction mixture was observed. The saponification of the ester was continued for 12-14 hours. Gradually the reaction mass turned yellow and there separated 6 g of the white potassium β,β-pentamethyleneglycidate. The salt was filtered, washed with alcohol and recrystallized twice from anhydrous alcohol. White lamellar crystals were obtained, insoluble in the cold in the ordinary organic solvents, difficultly soluble in cold alcohol and readily soluble in hot alcohol.

0.1497 g sub.: 0.0667 g K_2SO_4. 0.3662 g sub.: 0.1627 g K_2SO_4. Found %: K 20.0, 19.96. $C_8H_{11}O_3K$. Calculated %: K 20.08.

β,β-Pentamethyleneglycidic Acid (X). To a water solution of the potassium β,β-pentamethyleneglycidate was added with cooling a 1% hydrochloric acid solution to acid reaction to Congo. A white lustrous precipitate of β,β-pentamethyleneglycidic acid separated, which was filtered and dried in a vacuum desiccator; m.p. 61-62°. After recrystallization from aqueous methanol the melting point dropped to 46-47°. Long exposure to the air at room temperature transformed the β,β-pentamethyleneglycidic acid into a viscous, dark, tarry mass.

3,3-Pentamethyleneglycidol (V). In a three-necked flask, fitted with stirrer, reflux condenser, dropping funnel and thermometer, and protected from atmospheric moisture by means of calcium chloride tubes, was placed a solution of 15.76 g of ethyl β,β-pentamethyleneglycidate in anhydrous ether. The mixture was cooled to −65° by means of acetone-dry ice mixture. To the cooled solution with vigorous stirring was cautiously added dropwise a solution of 1.72 g of 95% lithium aluminum hydride in 245 ml of anhydrous ether. The ether solution was added at such a rate that the reaction mixture temperature stayed at −65° during the whole experiment. The addition of the lithium aluminum hydirde solution required 2-2.5 hours. The mixture was let stand in the cooling bath, the temperature of which was gradually raised to −30°. The reaction mass was kept at this temperature for 1 hour. Then the temperature was raised to −10° and there was added 6 ml of ethyl acetate (for decomposing the excess lithium aluminum hydride), 48 ml of saturated ammonium chloride solution and several milliliters of water. The ether was separated, while the water solution was additionally ether extracted. The ether solution was dried over fused magnesium sulfate. After removal of solvent the residual oil was vacuum distilled.

There was obtained 10.75 g of substance with b.p. 120-123° at 10 mm, which corresponds to 88.5%. After a second distillation the b.p. was 116-117° at 9-10 mm. 3,3-Pentamethyleneglycidol is a mobile liquid without color or odor, soluble in the ordinary organic solvents and insoluble in water.

n_D^{17} 1.4823, d_4^{17} 1.0582, MR_D 38.33; calculated 37.91.
5.047 mg sub.: 12.525 mg CO_2; 4.475 mg H_2O. 3.297 mg sub.: 8.141 mg CO_2; 2.9B mg H_2O. 18.210 mg sub.: 3.14 ml CH_4 (22°, 752 mm). Found %: C 67.72, 67.39; H 9.92, 9.90; [H˚] 0.71. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.92; [H˚] 0.71.

1,1-Pentamethyleneglycerol (III) from 3,3-Pentamethyleneglycidol. To 1.55 g of 3,3-pentamethyleneglycidol was added 50 ml of 2% acetic acid solution with almost complete solution being observed. The mixture was heated for 1 hour on the boiling water bath and after cooling was ether extracted. Evaporation of the water gave 1.45 g of 1,1-pentamethyleneglycerol as white crystals. Yield 83%. After recrystallization from ethyl acetate the m.p. was 113-114°. The substance failed to depress the melting point when mixed with authentic 1,1-pentamethyleneglycerol.

1,1-Pentamethyleneglycerol 2,3-Diacetate from 1,1-Pentamethyleneglycerol. To a solution of 6 g of pentamethyleneglycerol in 60 ml of anhydrous pyridine was added 15.3 g of acetic anhydride. The mixture stood for 16 hours at room temperature, after which it was poured into 15 volumes of water. The solution was acidified with dilute hydrochloric acid until acid to Congo and then extracted with ether. The ether solution was washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After distilling off the ether there was obtained 7.48 g of substance with b.p. 127-128° at 2-2.5 mm.

1,1-Pentamethyleneglycerol 2,3-diacetate is a colorless, clear, viscous, oily liquid, readily soluble in the ordinary organic solvents and difficultly soluble in water.

n_D^{19} 1.4695, d_4^{19} 1.125, MR_D 60.50; calculated 60.25.
3.617 mg sub.: 7.853 mg CO_2; 2.708 mg H_2O. 16.996 mg sub.: 1.71 ml CH_4 (20°, 734 mm). Found %: C 59.25; H 8.37; [H'] 0.41. $C_{12}H_{20}O_5$. Calculated %: C 59.00; H 8.25; [H'] 0.41.

SUMMARY

1. The synthesis of 1,1-pentamethyleneglycerol was accomplished by two methods:

a) from cyclohexanone via 1-ethynylcyclohexanol, 1-vinylcyclohexanol, 1,1-pentamethyleneglycidol and 1,1-pentamethyleneglycerol monoacetate;

b) from cyclohexanone via the ethyl ester of β,β-pentamethyleneglycidic acid and 3,3-pentamethyleneglycidol.

2. On the example of converting the ethyl ester of β,β-pentamethyleneglycidic acid into 3,3-pentamethyleneglycidol it was shown that the esters of glycidic acids can be reduced by lithium aluminum hydride to the corresponding alcohols with retention of the α-oxide ring.

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SYNTHESES BASED ON ANABASINE

IX. SULFONATION OF N-ACETYL- AND N-METHYLANABASINE WITH SULFURIC ACID

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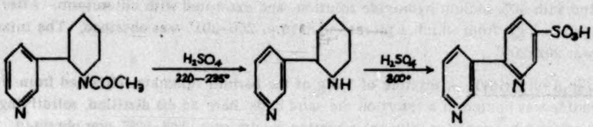
After the behavior of anabasine in its reaction with sulfuric acid [1] had been elucidated under the conditions used for pyridine sulfonation [2,3] it appeared of interest to study this reaction on some anabasine derivatives. The present paper communicates the study results obtained for the sulfonation of N-acetyl and N-methylanabasine.

The reaction of N-acetylanabasine with sulfuric acid under the conditions for the sulfonation of anabasine led to the formation of a crystalline product with acidic properties. A more detailed study revealed that the sulfonation of N-acetylanabasine proceeds in two stages – first the acetyl group is saponified and then, as in the case of anabasine, the 5-sulfonic acid of α,β-dipyridyl is obtained.



The sulfonation products of anabasine and N-acetylanabasine were identified as the nitriles (obtained from the sulfonic acid) and their derivatives. It should be mentioned that the reaction of N-acetylanabasine with sulfuric acid is much faster than the corresponding reaction for anabasine and the yield of product is slightly greater.

The experiments on the sulfonation of N-methylanabasine, made under the same conditions as for the sulfonation of anabasine and N-acetylanabasine, failed to give positive results. The reaction was accompanied by pronounced tarring and decomposition. Only volatile sulfur-containing products were isolated from the reaction mixture. The N-methylanabasine, as in the case of its electrochemical oxidation [4], proved to be less stable than anabasine to the action of sulfuric acid. Apparently, the presence of a methyl group on nitrogen lowers the stability of the piperidine ring. The negative experiments on the sulfonation of N-methylanabasine are indirect evidence of the fact that in the analogous reaction with anabasine the sulfonic group enters the dehydrogenated piperidine ring and the 5-sulfonic acid of α,β-dipyridyl is formed, i.e., the hydrogens of the piperidine ring fail to participate in the exchange reaction.

We made some additional studies on the properties of the 5-sulfonic acid of α,β-dipyridyl, which studies permitted us to elucidate some of its peculiarities when compared with β-pyridine-sulfonic acid. In contrast to the latter [3], the sulfonic group in α,β-dipyridyl-5-sulfonic acid is extremely stable. The exchange reactions proceed under more drastic conditions than in the case of β-pyridinesulfonic acid. Thus, for example, the fusion reactions with alkali and potassium cyanide do not proceed under conditions analogous to those required for β-pyridinesulfonic acid. The acid hydrolysis of α,β-dipyridyl-5-sulfonic acid, which we attempted under various conditions, could not be achieved. Apparently, the presence of a pyridyl radical in the para position influences the properties of the sulfonic group, endowing it with greater stability than it possesses in the pyridine ring.

A cursory attempt was made to obtain the corresponding amide from 5-cyano-α,β-dipyridyl by treating it with hydrogen peroxide [5]. This amide, being a derivative of nicotinamide, is of interest from the viewpoint of its physiological activity. However, the oxidation went further and the α,β-dipyridyl-5-carboxylic acid was formed instead.

EXPERIMENTAL

Acetylation of Anabasine. To 100 g of anabasine with cooling was gradually added 70 g of acetic anhydride. The resulting mixture was heated on the water bath for 12 hours. Then the reaction mass was dissolved in a small volume of water, saturated with soda, and extracted with chloroform. After drying over sodium sulfate and distilling off the solvent the residual oil was distilled in vacuo. Two fractions were obtained: 1st fraction - b.p. 129-132° (2 mm), 15.6 g (anabasine); 2nd fraction - b.p. 159-160° (2 mm), 61.5 g, n_D^{20} 1.5530 (N-acetylanabasine). N-Acetylanabasine picrate has m.p. 184-185°.

Sulfonation of N-Acetylanabasine with Sulfuric Acid at 300°. Experiment 1. To 30 g of N-acetylanabasine with cooling was added 33 ml of sulfuric acid (d 1.84). The obtained mixture was heated at 300° on the sand bath for 4 hours. After cooling the reaction mixture was dissolved in water and boiled with barium carbonate for 1 hour. The filtrate after removal of the mixed barium sulfate-barium carbonate precipitate was evaporated to small volume on the water bath. On cooling the barium salt of α,β-dipyridyl-5-sulfonic acid separated. Weight 12.7 g (27.8%).

Experiment 2. To 15 g of N-acetylanabasine with cooling was added 16 ml of sulfuric acid (d 1.84). Heating of the mixture to 220° gave a small amount of distilled acetic acid (reaction with ferric chloride). Then the heating was continued at 300° for 10-12 hours. The reaction product was dissolved in water and boiled with barium carbonate. The filtrate after removal of the mixed barium sulfate-barium carbonate precipitate was boiled with animal charcoal. The solution was filtered and evaporated to small volume; cooling gave a precipitate. The yield of the barium salt of α,β-dipyridyl-5-sulfonic acid was 7.8 g (34.2%). α,β-Dipyridyl-5-sulfonic acid was obtained from the barium salt by decomposition with sulfuric acid.

62.791 mg sub.: 2.69 ml NaOH (0.09775 N). Found: equiv. 238.8. $C_{10}H_7SO_3H$. Calculated: equiv. 236.0.

Saponification of N-Acetylanabasine with Sulfuric Acid. To 5 g of N-acetylanabasine was added in small portions 5.5 ml of sulfuric acid (d 1.84). The mixture was heated at 220-235° for 4 hours, then it was dissolved in 65 ml of water, neutralized with 30% sodium hydroxide solution, and extracted with chloroform. After distilling off the chloroform an oil remained (3.1 g), from which a picrate with m.p. 200-201° was obtained. The mixed melting point with anabasine picrate was 202-203°.

5-Cyano-α,β-dipyridyl. A mixture of 1.5 g of the barium sulfonate, obtained from N-acetylanabasine, and 3 g of potassium cyanide was heated in a retort on the sand bath; here an oil distilled, solidifying in the retort tube. After recrystallization from benzene (or toluene) a substance with m.p. 106-108° was obtained. The mixed melting point with 5-cyano-α,β-dipyridyl failed to be depressed and was 106-108°.

5-Cyano-α,β-dipyridyl Picrate. The picrate with m.p. 180-181° was obtained by mixing alcohol solutions of the nitrile and picric acid. The mixed melting point with authentic 5-cyano-α,β-dipyridyl was 179-181°.

5-Cyano-α,β-dipyridyl Methiodide. To 0.1 g of the nitrile in 5 ml of anhydrous alcohol was added 0.1 g of methyl iodide. A precipitate separated from the solution on standing. The methiodide, recrystallized from methyl alcohol, has m.p. 242-243°. The mixed melting point with authentic 5-cyano-α,β-dipyridyl failed to be depressed and was 242-244°.

Oxidation of 5-Cyano-α,β-dipyridyl with Hydrogen Peroxide. To 1 g of 5-cyano-α,β-dipyridyl in 5 ml of alcohol was added 3.3 ml of 30% hydrogen peroxide and then (to the slightly warmed solution) 0.9 ml of 24% sodium hydroxide solution. A violent reaction ensued and the reaction mixture was cooled. Then the mixture was heated on the water bath for 1.5 hours and after cooling was neutralized with 5% sulfuric acid; here an acidic precipitate with m.p. 278-280° was obtained. The mixed melting point with α,β-dipyridyl-5-carboxylic acid failed to be depressed and was 279-280°.

SUMMARY

1. The sulfonation of N-acetyl- and N-methylanabasine was studied under the conditions used for the sulfonation of pyridine and anabasine. It was established that the sulfonation of N-acetylanabasine yields the α,β-dipyridyl-5-sulfonic acid. N-Methylanabasine when reacted with sulfuric acid suffers profound changes.

2. It was shown that at 220-235° the acetyl group in N-acetylanabasine is saponified by sulfuric acid.

3. The oxidation of 5-cyano-α,β-dipyridyl with hydrogen peroxide gives the α,β-dipyridyl-5-carboxylic acid.

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ALKYLATION IN WATER MEDIUM IN THE PRESENCE OF QUATERNARY AMMONIUM SALTS

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Quaternary ammonium salts, containing the radicals: benzyl [1], alkoxymethyl [2], indolylmethyl [3], 3-chlorobutenyl [4] and others, possess alkylating properties. This, apparently, is due to the ability of quaternary ammonium salts to suffer cleavage. As yet only solitary radicals are known that are capable of alkylation; however, this speaks only for the lower bond stability of these radicals with the ammonium nitrogen and says nothing about whether it is possible to accomplish this reaction (alkylation) with other radicals.

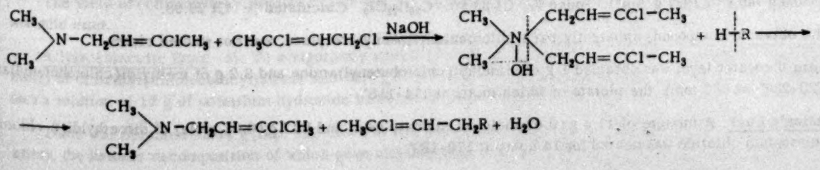
The excellent N-alkylation results obtained by us with dimethyldi(3-chlorobutenyl)ammonium chloride [4] permitted the hope that this salt would also prove to be a C-alkylation agent for compounds with labile hydrogen atoms. We subjected the compounds fluorene, naphthalene, phenylacetylene, malonic and acetoacetic esters to many hours of heating with dimethyldi(3-chlorobutenyl)ammonium chloride. The first two compounds under such heating remained unchanged and the only thing that happened in the reaction mixture was the earlier observed transformation of the dimethyldi(3-chlorobutenyl)ammonium chloride itself [5]. Phenylacetylene, malonic ester and acetoacetic ester actually underwent alkylation.

It seemed probable that alkylation would also proceed in alkaline medium, i.e., with quaternary ammonium bases. And since the formation of dimethyldi(3-chlorobutenyl)ammonium chloride from dimethyl(3-chlorobutenyl)amine and 1,3-dichloro-2-butene proceeds very rapidly, we deemed it possible to take it (the ammonium salt) in catalytic amounts and have in the reaction mixture a sufficient amount of 1,3-dichloro-2-butene so that the dimethyl(3-chlorobutenyl) amine liberated as the result of alkylation would immediately be bound by the 1,3-dichloro-2-butene with the repetitive formation of dimethyldi(3-chlorobutenyl)ammonium chloride. As a result, the tertiary amine would play the role of catalyst – a transfer agent for the chlorobutenyl radical.

Experiment completely justified our expectations. Acetoacetic ester in the presence of catalytic amounts of dimethyl-(3-chlorobutenyl)amine with the gradual addition of aqueous alkali is alkylated by 1,3-dichloro-2-butene. The yield of 3-chlorobutenylacetoacetic ester, based on the amount of acetoacetic ester taken, was 58%. The reaction proceeds smoothly and is complete after 15-25 minutes; acetylacetone also alkylates well, while malonic ester is alkylated in poorer yield. The replacement of 1,3-dichloro-2-butene by similarly constituted alkyl halides – allyl bromide and benzylchloride – failed, as was to be expected, to change the result.

It was shown by Knunyants [6] that the alkylation of acetoacetic ester with dialkyl sulfates can be run in water medium; for this reason we ran some control experiments on the alkylation of acetoacetic ester with 1,3-dichloro-2-butene in water medium in the absence of dimethyl(3-chlorobutenyl)amine. The (3-chlorobutenyl)acetoacetic ester was formed in an 18% yield of the theoretical. This sharp difference in yields clearly speaks for the catalytic influence exerted by the tertiary amine.

We assumed that also under these conditions the alkylation proceeds through the quaternary compound and that we are dealing with a reaction that is analogous to Hofmann reaction for the cleavage of quaternary bases, the only difference being that the hydrogen is taken not from the cleaved radical (which leads to an unsaturated compound) but from the compound with labile hydrogen atom that is present in the reaction mixture, which leads to its alkylation:



$$(CH_3)_2N-CH_2CH=CClCH_3 + CH_3CCl=CHCH_2Cl \xrightarrow{NaOH} (CH_3)_2\overset{+}{N}(OH^-)(CH_2CH=CCl-CH_3)_2 + H-R \longrightarrow$$

$$\longrightarrow (CH_3)_2N-CH_2CH=CClCH_3 + CH_3CCl=CH-CH_2R + H_2O$$

However, as further studies revealed, our representations on the reaction mechanism proved to be at variance with actuality, although they led us to some positive results.

Desiring to confirm the reaction mechanism adopted by us for alkylation in aqueous medium, we ran an experiment on the alkylation of acetoacetic ester with an aqueous solution of dimethyldi(3-chlorobutenyl)ammonium hydroxide without the addition of alkyl halide. The alkylation of acetoacetic ester failed to proceed under these conditions. The original postulation that the presence of a large amount of ammonium base in some way hinders alkylation was not confirmed: the presence of an equimolar amount of the ammonium base fails to hinder alkylation by the alkyl halide.

Later, in order to verify if the alkylation proceeds through the quaternary compound, we ran the following two experiments: 1) alkylation of acetoacetic ester with 1,3-dichloro-2-butene in the presence of an equimolar amount of dimethyldibenzylammonium chloride, and 2) alkylation of acetoacetic ester with benzyl chloride in the presence of an equimolar amount of dimethyldi(3-chlorobutenyl)ammonium chloride.

In the first experiment we obtained the pure (chlorobutenyl)acetoacetic ester (and its decomposition product – 6-chloro-5-hepten-2-one), and in the second – pure benzylacetoacetic ester (and its decomposition product – benzylacetone).

The results of these two experiments show that acetoacetic ester is alkylated only by the added alkyl halide. The alkyl radicals, present in the quaternary salt, do not participate in the alkylation (under these conditions).

In the literature we found one reference to the catalytic influence of quaternary ammonium salts in the synthesis of esters and derivatives of benzyl cyanide [7]. The author of these studies postulates that in these reactions there are formed, as intermediates, compounds that are analogous to those isolated by Schlenk and Holtz [8], namely, organic tetraalkylammonium derivatives. It seems very probable to us that a quaternary ammonium salt in alkaline medium forms with the alkylating compound an intermediate tetraalkylammonium derivative, which, similar to the analogous sodium derivative, reacts further with the added alkyl halide.

EXPERIMENTAL

Alkylation with Dimethyldi(3-chlorobutenyl)ammonium Chloride

Fluorene. A mixture of 16.6 g (0.1 mole) of fluorene and 25.9 g (0.1 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 30 hours at 160-170°. Then the reaction mixture was diluted with water and extracted with ether. The ether extract was dried over calcium chloride and after distilling off the solvent the residue was vacuum distilled. There was obtained 15.8 g of crystals, melting at 110-112°, and in mixture with fluorene at 111-113°. The water layer was made alkaline and washed with ether. The ether extract after distilling off the ether was distilled. There was obtained 3.7 g of dimethyl-(chlorobutenyl)amine and 3.1 g methyldi(chlorobutenyl)amine [5], the picrate of the latter melts at 114-115° and fails to depress the melting point when mixed with the picrate of methyldi(chlorobutenyl)amine. The gas liberated in the alkalization of the water layer was passed into dilute hydrochloric acid, which was then evaporated. The residue, recrystallized from alcohol, melts at 271-273° and fails to depress the melting point when mixed with trimethylamine hydrochloride.

Naphthalene. A mixture of 12.8 g of naphthalene (0.1 mole) and 25.9 g (0.1 mole) of dimethyldi(3-chlorobutenyl) ammonium chloride was heated for 48 hours at 170-175°. As the result of treatment, analogous to the preceding, there was obtained 11.7 g of naphthalene and the transformation products of the quaternary salt.

Phenylacetylene. A mixture of 10.2 g (0.1 mole) of phenylacetylene and 25.9 g (0.1 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 14 hours at 160-165°. The reaction mixture was diluted with water, extracted with ether, and after distilling off the solvent was vacuum distilled. There was obtained 7.9 g (fraction with b.p. 42-50° at 14 mm) of unreacted phenylacetylene and 7.4 g of a liquid with b.p. 163-166° at 14 mm, failing to give a precipitate with ammoniacal silver nitrate solution.

0.1019 g sub.: 0.1227 g AgCl. Found %: Cl 29.80. $C_{20}H_{21}Cl_3$. Calculated %: Cl 28.98.

The obtained compound, apparently tri(3-chlorobutenyl)phenylacetylene, was not studied closer.

From the water layer was obtained 1 g of dimethyl(chlorobutenyl)amine and 3.2 g of methyldi(chlorobutenyl)amine (b.p. 222-230° at 680 mm), the picrate of which melts at 114-115°.

Malonic Ester. A mixture of 11.4 g (0.07 mole) of malonic ester and 20.7 g (0.08 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 14 hours at 170-180°.

There was obtained 3.9 g (22.6%) of the (chlorobutenyl)malonic ester (b.p. 165-168° at 19 mm), possessing after a second distillation the following constants:

b.p. 144.5-145° (11 mm), d_4^{16} 1.1093, n_D^{16} 1.4523.

From the literature [9]: b.p. 121.5-122.5° (6 mm), d_4^{16} 1.1059, n_D^{16} 1.4536.

Acetoacetic Ester. A mixture of 26 g (0.2 mole) of acetoacetic ester and 51.7 g (0.2 mole) of dimethyldi(3-chlorbutenyl)ammonium chloride was heated for 14 hours at 155-160°.

There was obtained 16.1 g (b.p. 144-147° at 16 mm) of the (chlorobutenyl)acetoacetic ester of 37.0%, based on taken acetoacetic ester. Part of this fraction was decomposed to the ketone. There was obtained the 6-chloro-5-hepten-2-one with b.p. 189-192° at 680 mm, and giving the semicarbazone with m.p. 123-125°.

From the literature [10]: b.p. 188-190°, semicarbazone m.p. 125-126°.

Alkylation in Water Medium

(Chlorobutenyl)acetoacetic Ester. To a vigorously stirred mixture of 26 g (0.2 mole) of acetoacetic ester, 27.5 g (0.22 mole) of 1,3-dichloro-2-butene and 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine, heated on the water bath, was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. The heating was continued another 5 minutes. The top layer and the ether extract of the lower layer were dried over calcium chloride, and after distilling off the solvent, were distilled in vacuo. There was obtained 5.8 g of unreacted acetoacetic ester and 25.5 g (b.p. 127-137° at 8 mm) of the (chlorobutenyl)acetoacetic ester, the ketonic decomposition of which gave 10.1 g (34.4%) of 6-chloro-5-hepten-2-one, boiling at 189-192° and giving a semicarbazone with m.p. 123-125° [10].

The yield of (chlorobutenyl)acetoacetic ester, based on taken acetoacetic ester, was 58.3%, and 75.1%, based on reacted acetoacetic ester.

The water layer was acidified with hydrochloric acid and again extracted with ether. Nothing was found in the ether extract.

Under analogous conditions in the presence of 0.002 mole of catalyst the yield of (chlorobutenyl)acetoacetic ester was 46.0%, in the absence of catalyst it was 18.4%.

(Chlorobutenyl)acetylacetone. To a vigorously stirred mixture of 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine, 2.5 g (0.02 mole) of 1,3-dichloro-2-butene and 20 g (0.02 mole) of acetylacetone on the water bath was added over 30 minutes 25 g (0.2 mole) of 1,3-dichloro-2-butene and 11.2 g of potassium hydroxide in 15 ml of water. Heating was continued for another 30 minutes. There was obtained 5.9 g of unreacted acetylacetone and 20.3 g (b.p. 110-115° at 6 mm) of (chlorobutenyl)acetylacetone, possessing after a second distillation the following constants:

B.p. 108-109° (4 mm), d_4^{20} 1.0967, n_D^{20} 1.489, MR_D 49.6. $C_9H_{13}O_2ClF$. Calculated: 48.18.
0.1028 g sub.: 0.0776 g AgCl. Found %: Cl 18.68. $C_9H_{13}O_2Cl$. Calculated %: Cl 18.3.

The yield of (chlorobutenyl)acetylacetone was 54%, based on taken acetylacetone, and 77.3%, based on consumed acetylacetone.

(Chlorobutenyl)malonic Ester. To a vigorously stirred mixture of 5.4 g (0.04 mole) of dimethyl(chlorobutenyl)amine, 55 g (0.44 mole) of 1,3-dichloro-2-butene and 64 g (0.4 mole) of malonic ester on the water bath was added over 20 minutes a solution of 24 g of potassium hydroxide in 40 ml of water. Heating was continued for another 5 minutes.

There was obtained 25.77 g (b.p. 185-193° at 680 mm) of unreacted malonic ester and 29.92 g (b.p. 144-150° at 10 mm) of (chlorobutenyl)malonic ester, possessing the following constants [9]:

B.p. 144.5-145° (11 mm), d_4^{16} 1.1093, n_D^{16} 1.4523.

The yield of (chlorobutenyl)malonic ester was 30.1%, based on taken malonic ester, and 50.4%, based on consumed malonic ester.

Allylacetoacetic Ester. a) To a vigorously stirred mixture of 26 g (0.2 mole) of acetoacetic ester, 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine and 26.7 g (0.2 mole) of allyl bromide on the water bath was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 5 minutes.

There was obtained 22.44 g (b.p. 196-206° at 680 mm) of allylacetoacetic ester (66%, based on taken acetoacetic ester), the ketonic decomposition of which gave allylacetone, b.p. 124-126° at 680 mm, giving a semicarbazone with m.p. 96-97° (literature [11], b.p. 129.6°; m.p. of semicarbazone 99-100°).

b) Under similar conditions without catalyst there was obtained 16.24 g (b.p. 195-205° at 680 mm) of the allylacetoacetic ester (47.7%, based on taken acetoacetic ester), the ketonic decomposition of which gave allylacetone, giving a semicarbazone with m.p. 94-96°.

Benzylacetoacetic Ester. a) To a vigorously stirred mixture of 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine, 2.53 g (0.02 mole) of benzyl chloride and 26 g (0.2 mole) of acetoacetic ester on the water bath was added over 25 minutes 25.3 g of benzyl chloride and 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 35 minutes.

The following fractions were obtained (at 8 mm): 1st) 80-85°, 8.3 g; 2nd) 85-145°, 1.8 g; 3rd) 145-150°, 22.0 g; 4th) 205-213°, 6.1 g.

To the 1st fraction was added aqueous alkali solution. A voluminous precipitate separated. Then water was added and the mixture was extracted with ether. There was obtained 3.5 g of pure benzyl chloride.

The fraction with b.p. 145-150° (at 8 mm) distilled at 274-276° at atmospheric pressure (680 mm).

Prolonged standing of this fraction with aqueous ammonia gave needlelike crystals,after recyrstallization from water melting at 149-150°. The m.p. given in the literature [12] for benzylacetoacetic ester is 283-284°. With ammonia the benzylacetoacetic ester gives the amide of benzylacetoacetic acid, melting at 150-151°.

The yield of benzylacetoacetic ester was 52.2%, based on taken acetoacetic ester, and 64.4%, based on consumed acetoacetic ester.

The use of benzyl iodide instead of the chloride failed to significantly affect theyield of the benzylacetoacetic ester.

b) Under analogous conditions without catalyst the yield of benzylacetoacetic ester was 32.3%, based on taken acetoacetic ester, and 42%, based on consumed acetoacetic ester.

Acetoacetic Ester and Dimethyldi(3-chlorobutenyl)ammonium Hydroxide. To a solution of 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride in 12 ml of water was added a solution of 12 g of potassium hydroxide in 20 ml of water. Then 26 g (0.2 mole) of acetoacetic ester was added and the reaction mixture was stirred for 25 minutes on the water bath. There was obtained 20.0 g of pure acetoacetic ester with b.p. 69-72° (8 mm). Acidification of the water layer and ether extraction gave another 0.8 g of acetoacetic ester.

Alkylation of Acetoacetic Ester in the Presence of an Equimolar Amount of Dimethyldi(3-chlorobutenyl)ammonium Hydroxide. To a solution of 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride in 12 ml of water was added a solution of 12 g of potassium hydroxide in 20 ml of water. Then was added 25 g (0.2 mole) of 1,3-dichloro-2-butene and 26 g (0.2 mole) of acetoacetic ester. To the obtained mixture with vigorous stirring on the water bath was added over 15 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 10 minutes.

There was obtained 24.5 g of (chlorobutenyl)acetoacetic ester with b.p. 114-124° at 5 mm (56.1%, based on taken acetoacetic ester).

Alkylation of Acetoacetic Ester with 1,3-Dichloro-2-butene in the Presence of an Equimolar Amount of Dimethylbenzylammonium Chloride. To 52.3 g (0.2 mole) of dimethylbenzylammonium chloride was added a solution of 9 g of sodium hydroxide in 40 ml of water. To the obtained solution was added 26 g (0.2 mole) of acetoacetic ester and 25 g (0.2 mole) of 1,3-dichloro-2-butene. To the vigorously stirred mixture on the water bath was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 5 minutes.

There was obtained 18.2 g (41.6%) of the (chlorobutenyl)acetoacetic ester (b.p. 125-135° at 7 mm) and 2.4 g (8.2%) of 6-chloro-5-hepten-2-one, which distilled without vacuum in the range 187-196° and which gave a semicarbazone with m.p. 123-125°.

Alkylation of Acetoacetic Ester with Benzyl Chloride in the Presence of an Equimolar Amount of Dimethyldi(3-chlorobutenyl)ammonium Chloride. To a solution of 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was added a solution of 9 g of sodium hydroxide in 20 ml of water. To the obtained base was added 26 g (0.2 mole) of acetoacetic ester and 25.3 g (0.2 mole) of benzyl chloride. To the obtained mixture, vigorously stirred on the water bath, was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 5 minutes.

There was obtained 15.8 g (35.9%) of benzylacetoacetic ester (b.p. 132-142° at 4 mm) and 3.6 g (12.2%) of benzylacetone (b.p. 223-228° at 680 mm), giving a semicarbazone with m.p. 142°. The literature [13] m.p. for benzylacetone semicarbazone is 142°.

SUMMARY

1. In the presence of catalytic amounts of quaternary ammonium salts it is possible to affect alkylation of compounds, containing a labile hydrogen, with alkyl halides in water medium under the influence of aqueous alkali.

2. The alkylation proceeds exclusively on the basis of the added alkyl halide. Under our conditions the alkyl radicals, present in the taken quaternary ammonium salt, fail to participate in the alkylation.

3. In its mechanism this alkylation reaction is completely different from the reaction mechanism for the alkylation of quaternary ammonium salts in nonaqueous media at elevated temperatures.

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There was obtained 13.8 g (73.5%) of [illegible] (b.p. 130-140°) and 7.0 g [illegible] of benzalacetone (b.p. 252-258° at 760 mm), giving a semicarbazone with m.p. 142°. The literature [13] says the benzalacetone semicarbazone is 142°.

SUMMARY

1. In the presence of catalytic amounts of quaternary ammonium salts it proves possible to alkylate [illegible] compounds, containing a labile hydrogen, with allyl halides in water medium under the influence of caustic alkalis.

2. The alkylation proceeds exclusively at the expense of the added alkyl halide, [illegible] the alkyl radicals present in the taken quaternary ammonium salt fail to participate in the alkylation.

3. In its mechanism this alkylation reaction is completely different from the reaction [illegible] by the alkylation of quaternary ammonium salts in homogeneous media at elevated temperatures.

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IN MEMORIUM ROBERT KARLOVICH EIKHMAN

A. I. Korolev

On October 30, 1958 R. K. Eikhman died; Doctor of Technical Sciences, one of the greates specialist and organizers of the aniline dye industry.

Robert Karlovich was born in 1879 in the home of a public teacher, in the village Lesnoi Karamysh of the Saratov district. After completing high school R. K. was a grammar school teacher for three years. In 1907 R. K. received a Chemical Engineering Degree and joined the Joint-Stock Company Plant in Moscow (later the Derbenevsk Plant). From the autumn of 1914 R. K. was the director of this plant, and after the nationalization of the latter in 1919 he became the first chosen Red director of this plant. The outstanding role played by R. K. in developing the plant during this time is covered in a feature article appearing in the November 30, 1922 issue of the newspaper "Pravda". In 1923 he occupied one of the first places in the number of 12 directors recognized by decree of the All-Russian jury under Chairman Mary Ilinichny Ulyanova ("Pravda" newspaper of February 9, 1923).

In 1919 R. K. was chosen a member of the committee for the administration of the aniline dry industry and assumed in succession the duties of Head of the Technical Section, Chairman of the Technical Committee of the industry and Substitute Director.

Up to 1925 R. K. also retained his directorship duties at the Derbenevsk plant. From 1925 to 1938, remaining on directive work in the Supreme administration of the industry, R. K. devoted great attention to the operation of the Central Laboratory of the industry and to the Experimental Plant; only from 1938, after a serious illness, was R. K. forced to limit his work to the confines of the industry's institute (the K. E. Voroshilov Scientific Institute of Organic Intermediates and Dyes).

The services of R. K. in developing the native industry are exclusively great. Even in the First World War, in 1915, R. K. organized in Moscow the production of phenol, picric acid and trotyl (trinitrotoluene)—materials that were deficient at the time and extremely important products in time of war. During these years, R. K. acted as consultant on the design, construction and familiarization with the production of these products at the plants near Moscow, in the Don Basin and around Petrograd.

In the period after the Great October Socialistic Revolution R. K. again entered into the role of director and organizer of many new Soviet industries.

As far as the more important achievements of R. K. are concerned, mention should be made of the original and highly productive method created by him for the production of phenol, which method, together with other methods, is used in our plants. Of no less significance for the national economy were the investigations of R. K. on the fractional separation of the coal tars from the Don and Kuznets Basins, and especially the work done on the anthracene-containing fractions. R. K. discovered and introduced into industry the dive-colored dyes, which are widely used in the textile industry (newspaper "Izvestiya" of February 15, 1939).

The researches of R. K. bore important significance for aniline, 2-naphthol, sulfur black, many kinds of sulfur dyes, anthraquinone, benzidine, alizarin and many others.

A great service of R. K. was the organization of laboratories at the plants of the aniline dye industry, which laboratories were capable of conducting original independent studies. On the problems of organic raw materials, chemistry and technology of intermediates and dyes, R. K. published about 20 papers, in which number are included several patents.

For a number of years R. K. directed the studies of diploma candidates at the D. I. Mendeleev Moscow Chemical-Technological Institute. Many of the industry's leaders are students of R. K.

The great services of R. K. in the industry were recognized in 1935 by decree of the People's Commissar of Heavy Industry and in 1939 by the People's Commissar of the Chemical Industry. In 1953 R. K. was rewarded by the Presidium of the Supreme Council of the USSR with the Order of Lenin.

The name of Robert Karlovich Eikhman, dear to all workers in the aniline dye industry, will go down in the history of the creation and devleopment of the Soviet aniline dye industry.

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THE TWENTIETH ANNIVERSARY OF THE DISCOVERY OF ARTIFICIAL RADIOACTIVITY

A. P. Ratner

Twenty years have passed since one of the most important discoveries of the twentieth century – the discovery of artificial radioactivity by Frederic and Irene Joliot-Curie. While studying the transmutation of elements during their bombardment with alpha particles from polonium, the Joliot-Curies noticed that three elements – aluminum, boron and magnesium – emitted positrons under the action of polonium alpha particles. The radiation did not come to an end even after the cessation of the bombardment, and its intensity decreased exponentially with time in the same manner as that of natural radioactive elements. The Curies explained this phenomenon by the fact that, as a result of transformations caused by alpha particles in the nuclei of these elements, unstable radioactive nuclei decomposing with the emission of positrons were formed. They verified the correctness of their hypothesis by using the fact that the artificially obtained radioactive nuclei were different in their chemical properties from the elements which were bombarded.

Actually, the nuclear reactions which took place in the Curies' experiments can be written in the following form, taking into consideration the fact that neutrons are emitted in these reactions:

$$Al_{13}^{27} + He_2^4 \rightarrow P_{15}^{30} + n_0^1,$$

$$B_5^{10} + He_2^4 \rightarrow N_7^{13} + n_0^1,$$

$$Mg_{12}^{24} + He_2^4 \rightarrow Si_{14}^{27} + n_0^1.$$

The Joliot-Curies isolated the radioactive isotopes of phosphorus P^{30}, nitrogen N^{13}, and silicon Si^{27}, which were obtained as a result of these reactions, from the bombardment target, after having previously added small amounts of inactive isotopes of these elements, and showed that all the activity was concentrated in the added carriers. Thus, they were the first to artificially prepare and isolate new radioactive isotopes of ordinary elements which do not exist in the radioactive form in nature.

It would be hard to overestimate the value of the discovery of Frederic and Irene Joliot-Curie for all of modern science. It is sufficient to say that they provided the original impetus for investigations that led to the discovery of nuclear fission (to which, incidentally, the Curies also made a very important contribution) and to the possession of nuclear energy by humanity.

The discovery of artificial radioactivity had especially great significance for chemistry. It has made possible the extending of the field of application of radioactive methods in chemistry, previously limited by the framework of the natural radioactive elements, to the whole of the Periodic System.

The extraordinary sensitivity and specificity of radioactive methods (they can easily determine radioactive isotopes in quantities of 10^{-12} – 10^{-18} g in a great mass of extraneous matter, including inactive isotopes of the same element) have been used for a long time for the solving of a number of experimental problems in various fields of chemistry. It is sufficient to recall the synthesis of the hydrides of the heavy elements of the IV and V groups, carried out by Paneth, the determination of the coefficients of diffusion of lead in metal and in a number of salts, the investigation of the metabolism of lead and bismuth in the organism, etc. However, the greatest possibilities which radioactive methods open up for experimenters could not be utilized to a sufficient extent as long as their use was limited to the ten elements at the end of the periodic system for which natural radioactive isotopes are known.

After the discovery of artificial radioactivity the preparation of artificial radioactive isotopes of the stable elements became possible; at the present time, we have such isotopes for almost all elements in quantities sufficiently great for their wide utilization. Thanks to this, unlimited possibilities for the utilization of radioactive methods in various fields of chemistry have been opened up; in recent years they have found their widest use, their applications increasing with every year.

Even the most concise statement of all of the results achieved in chemistry through the use of artificial radioactive elements would be far too long, not only for this article, but even for a large monograph; we will therefore limit ourselves to the citation of some of the most important examples which will make it possible for us clearly to realize the importance of the use of artificial radioelements in chemistry.

First, it is necessary to cite the discovery of new chemical elements. Even the utilization of natural radioactive elements had made possible the discovery of a series of new elements, the radioactive isotopes of which were encountered in nature in insignificantly small quantities. These elements occupied the places which had been empty in the periodic system between bismuth and uranium, with the exception of the two elements with the atomic numbers 85 and 87 – ekacesium (astatine) and ekaiodine (francium).

The discovery of artificial radioactivity made possible a significant increase in the number of known elements and the extension of the borders of the periodic system, since it enabled us to obtain radioactive isotopes of previously unknown elements and to study their chemical properties by radioactive means. Certain new elements, e. g. plutonium and technetium, which were discovered and the chemical properties of which were first investigated by radioactive methods on insignificantly small quantities of them, were then isolated in weighable quantities and their chemical properties studied by ordinary chemical means; the conclusions made on the basis of radiochemical investigations were, as a rule, fully confirmed.

The first new transuranium elements, discovered through the use of the phenomena of artificial radioactivity, were neptunium, Np, Z = 93, and plutonium, Pu, Z = 94. They were discovered by American radiochemists in 1940-1944 among the artificial radioelements which were obtained by the bombardment of uranium with neutrons. Even the first work on the chemical properties of the newly discovered elements, carried out on the short lived isotopes Np^{239} and Pu^{238} on quantities on the order of $10^{-13}-10^{-14}$ g made possible the establishment of the great similarity between the chemical properties of the new elements and uranium. This led to the conclusion that the last elements of the periodic system begin a new group of elements which are analogous in their properties to the rare earth elements. The formation of this group is associated with the completing of the inner 5_f electron shell. Later investigation with weighable quantities of these elements fully confirmed this conclusion, and if there is still a difference of opinion among chemists on this question it is only on whether this group begins with actinium or uranium.

Soon, by means of the bombardment of uranium and plutonium with quickly moving deuterons and other heavy nuclei, Seaborg was able still further to extend the borders of the periodic system, discovering elements one after another; they were: Americium, Z = 95; curium, Z = 96; berkelium, Z = 97; californium, Z = 98; and finally, in 1951, afinium, Z = 99, and centurium, Z = 100. The discovery of the latter two elements was recently confirmed by American and Canadian scientists.

Artificial radioactivity made possible not only the extending of the borders of the periodic system to Z = 100, but also the filling of the empty places in it. After the discovery of rhenium and hafnium, there remained four empty places in the periodic system – the rare earth element Z = 61, ekamanganese, Z = 43, and the two elements mentioned above with Z = 85 and 87. By the selection of the corresponding nuclear reaction, radioactive isotopes of these elements were obtained; this made possible the study of their chemical properties. The isotopes of element number 43, which is called technetium since it was the first artificially obtained element (1937), have long lives ($Tc^{99}T = 2.1 \cdot 10^5$ years,, $Tc^{97}T = 10^4$ years), which made possible the isolation of weighable quantities of this element.

There is a great deal of interest in the chemical properties of element number 85, astatine, the heavy analog of the halogen group. This element, while remaining close in its properties to those of its nearest analog, iodine, differs considerably from it in that it is not a typical non-metal. In agreement with the general laws of the periodic system, basic properties are also manifested in astatine. Thus, for example, astatine is precipitated by hydrogen sulfide from acid solutions, and is evolved at the cathode upon electrolysis.

The use of artificial radioactive elements has opened completely new prospectives for chemistry in relation to one of its basic questions – the study of the chemical bond. Radioactive methods make possible the easy distinguishing of radioactive isotopes of a given element from each other and from inactive isotopes; therefore, through the use of radioactive elements (by the so-called "marked" atom method) it is possible to trace the process of movement of the same kind of atom from one molecule to another or between different positions in the same molecule. The study of the kinetics of such changes makes possible the obtaining of data on the mobility of atoms linked in the molecule in various ways. Thus, for example, A. A. Greenberg and co-workers studied the speed of exchange of central and peripheral atoms in various inorganic complex salts, and showed that exchange of peripheral atoms takes place quite quickly even in such stable complex salts as bromoplatinates and bromoplatinites, but that exchange of central atoms in complex compounds is practically absent.

Artificial radioactive elements have been widely used for the study of the equivalence of bonds in complex compounds (A. E. Polesitsky, Ya. A. Fialkov, Yu. P. Nazarenko), the mobility of halogen atoms in various organic compounds (the first work in this direction was done by S. Z. Roginsky and co-workers), etc. The use of artificial radioactive isotopes for the study of the mechanism of chemical reactions has proved very fruitful.

The use of artificial radioactivity has opened up great possibilities in analytical chemistry. The possibility of simple and easily determining radioactive elements in the presence of extraneous non-radioactive substances has made possible the study of the rate and degree of completenes of analytical separations. After adding very small quantities of its radioactive isotope to the element to be determined, it is possible to check its loss in all stages of analysis through its radioactivity and to make corrections in its quantity, if necessary. This use of radioactive isotopes as an indicator for the control of the degree of completeness of separation during complex analyses was first proposed by I. E. Starik in connection with the determination of the content of lead in its ores, and is today widely used in analytical chemistry.

The phenomena of artificial radioactivity are also successfully used directly for the determination of very small quantities of many elements. This use, so-called activation analysis, is based on the fact that the probability of neutron capture during the formation of radioactive isotopes varies greatly from element to element ($10^4 - 10^5$ times); therefore, by bombarding any element which is difficult to activate with a powerful neutron source and measuring the radioactivity which is obtained as a result, it is possible to determine very small quantities of strongly activated admixtures. The sensitivity and selectivity of activation analysis can be raised still more by means of the chemical separation of the radioactive elements which are formed after the addition of their inactive isotopes as carriers, and also by the correct selection of the length of bombardment and of the time lag between bombardment and the taking of measurements. Activation analysis makes possible the determination, for example, of $6 \cdot 10^{-9}$ g of manganese, $7 \cdot 10^{-9}$ g of sodium and gallium, $2 \cdot 10^{-9}$ g of scandium and arsenic, $3 \cdot 10^{-10}$ g of lanthanum, and $3 \cdot 10^{-11}$ g of europium and dysprosium. It has found practical use in America in the control of the chemical purity of germanium for radio-technical purposes, when the quantity of a number of admixtures must not rise above 10^{-6}%.

The use of artificial radioactive isotopes has proved very valuable in the analysis of complex mixtures of compounds which are difficult to separate; the method is called "isotope dilution". This method is based on the fact that different isotopes of the same element (with the exception of the hydrogen isotopes) are not separated from each other in ordinary chemical operations. Let us now introduce into the mixture to be analyzed, a mixture of amino acids obtained on hydrolysis of some protein for example, a certain quantity of one of the amino acids marked with the radioactive carbon isotope C^{14}, the specific activity of which (activity per mg) is known. After careful mixing the marked molecules are distributed equally among all the molecules of the given amino acid, and this distribution does not undergo any further change in the process of analysis; therefore, it is sufficient to separate an arbitrary part of the amino acid in the pure form and determine its specific activity in order to calculate the quantity of the given amino acid in the mixture, since the change in the specific activity is determined by the relationship between the amount of the amino acid which was added and the amount of it originally found in the mixture. This makes the quantative separation of the mixture unnecessary. The use of radioactive methods allowed A. L. Kursanov and his students to achieve important successes in the study of the processes of plant nutrition. They were able to prove that plants can assimilate carbon dioxide not only from atmospheric air through their leaves, but also through the root system from the air in the soil. They also succeeded in tracing further the course of synthesis of hydrocarbons and proteins from carbon dioxide in the plant. These results considerably deepened and broadened our knowledge of plant physiology, and will undoubtedy aid Soviet agro-biologists in the struggle to increase productivity, and for the creation of an abundance of agricultural products.

The examples which we have given far from exhaust all the uses of artificial radioactive isotopes in chemistry. In metallurgy, biology, medicine and electro-chemistry, the uses of radioactive methods, which were made possible by the Joliot-Curies' discovery have yielded and continue to yield new and more and more important and interesting results. We can point out with pride that among the scientists who have developed the use of artificial radioactivity in chemistry, Soviet chemists occupy a significant place.

REACTIONS BETWEEN ZIRCONIUM NITRATE AND THE IODATES OF THE ALKALI METALS IN SOLUTIONS

III. THE INFLUENCE OF THE ALKALI METALS ON THE COMPOSITION OF ZIRCONIUM IODATE AND ON REACTIONS IN WHICH PRECIPITATES ARE FORMED

M. I. Konarev and A. S. Solovkin

Earlier [1, 2], it was shown that zirconium hydroxyiodate was precipitated out when potassium iodate was added to a solution of zirconium nitrate. The precipitates had the following compositions: $Zr(OH)_3IO_3 \cdot 4H_2O$ and $ZrOH(IO_3)_3 \cdot 4H_2O$.

Upon long standing with mother liquors containing potassium iodate, hydroxyiodates which were amorphous in form, are crystallized, being transformed thereby into the hexaiodate – $Zr(IO_3)_4 \cdot 2KIO_3$, and the enaiodate – $Zr(IO_3)_4 \cdot 3KIO_3 \cdot 2HIO_3$. Ordinarily, a mixture is formed with varying contents of the hexa- and enaiodate. The composition of the mixture depends on the concentration of potassium iodate in the solution and on the acidity.

1. The Influence of the Concentration of the Hydrogen Ion and the Ions of Certain Alkali Metals on the Composition of the Zirconium Iodate Precipitate

The results described below were obtained with the utilization of iodic acid and the iodates of sodium, lithium, and rubidium as precipitating agents.

The quantity of zirconium in the original solution was equal to 1.386 g/l, and its content in the precipitate corresponded to 0.693 g/l or 0.0076 g-ion/l. Under these conditions, we obtained a zirconium iodate precipitate when potassium iodate was used. The preparation of the samples and their analysis were carried out by the methods described earlier [1].

The results obtained with iodic acid are given in Table 1, with sodium iodate – in Table 2, with lithium iodate – in Table 3, and with rubidium iodate – in Table 4. In these tables, only the composition of the precipitates which had settled from the solution for a long time is given, since the composition of the precipitating agent does not influence that of the freshly precipitated zirconium iodate.

On the addition of iodic acid, or of the iodates of the alkali metals (sodium, lithium, or rubidium) to a zirconium nitrate solution, hydroxyiodates are precipitated, as in the case of the addition of potassium iodate. From nitric acid solutions with a sufficiently high concentration of the precipitating agent, zirconium triiodate settles out. The form of the precipitate changes depending on the precipitating agent that is used. A more powdery residue is formed when potassium or rubidium iodate is used than when iodic acid or the iodates of sodium and lithium are employed as precipitants.

Iodic acid has a special significance in relation to the iodates of the alkali metals. Very concentrated solutions of these iodates may be prepared from iodic acid, while the solubility of the iodates of the alkali metals in water and in nitric acid is limited. If concentrated iodic acid is added to a solution of zirconium nitrate, at first a precipitate is formed; but when the concentration of iodic acid reaches approximately 0.75 M, the precipitate is fully dissolved. A further increase in the concentration of iodic acid stabilizes the solution.

Solutions of zirconium iodate in iodic acid are, evidently, colloidal in nature, since upon the addition of a small amount of a salt (potassium, ammonium, or aluminum nitrate), zirconium is precipitated in the form of a triiodate of the same composition as before its dissolution in iodic acid.

Upon long standing of triiodates with moderately concentrated solutions of iodic acid, and also with solutions of sodium, lithium, or rubidium iodates, the crystallization of the precipitate takes place; the same is true of solutions containing potassium iodate. The crystallization of zirconium iodate takes place more slowly in the presence of iodic acid and the iodates of sodium and lithium than it does in the presence of potassium and rubidium iodates. The precipitate is crystallized most quickly in the presence of rubidium iodate.

TABLE 1

Precipitating agent – iodic acid

Experiment No.	Concentration of HIO_3 in the solution (in moles/l)	Found in the precipitate (in %)			Ratio $Zr : IO_3$	Ratio of $K : Zr : IO_3$ with the same molecular concentrations of KIO_3
		Zr	IO_3	Sum		
		0.02 N HNO_3				
1	0.026	22.00	47.92	69.92	1 : 1.13	Not determined
2	0.068	17.36	62.03	79.39	1 : 1.89	0.16 : 1 : 1.60
3	0.103	11.50	82.54	94.04	1 : 3.74	0.49 : 1 : 2.35
4	0.164	11.42	84.20	95.62	1 : 3.84	0.61 : 1 : 2.51
5	0.294	11.11	84.12	95.23	1 : 3.94	Solution KIO_3 is lower.
6	0.476	The original precipitate has been fully dissolved.				
		0.5 N HNO_3				
7	0.053	10.69	81.10	91.79	1 : 3.97	1.49 : 1 : 5.34
8	0.109	11.42	80.73	92.15	1 : 3.70	2.06 : 1 : 6.81
9	0.200	11.97	80.25	92.22	1 : 3.49	2.6 : 1 : 8.0
10	0.501	10.71	85.32	96.03	1 : 4.11	Solution KIO_3 is lower.
		1.75 N HNO_3				
11	0.038	11.17	74.81	85.98	1 : 3.72	Not determined
12	0.090	12.07	79.23	91.30	1 : 3.42	1.93 : 1 : 5.86
13	0.180	11.32	80.28	91.60	1 : 3.69	2.43 : 1 : 7.85
14	0.311	11.28	82.68	93.96	1 : 3.81	2.57 : 1 : 8.07
15	0.584	11.24	84.63	95.87	1 : 3.94	Solution KIO_3 is lower.

TABLE 2

Precipitating agent – sodium iodate; acidity of the solution on HNO_3 0.5 N

Experiment No.	Concentration of $NaIO_3$ in the solution (in moles/l)	Found in the precipitate (in %)				Ratio $Na : Zr : IO_3$	Ratio of $K : Zr : IO_3$ with the same molecular concentrations of KIO_3
		Na	Zr	IO_3	Sum		
1	0.029	–	10.91	79.46	90.37	0 : 1 : 3.90	Not determined
2	0.097	–	10.62	80.86	91.48	0 : 1 : 3.96	2.08 : 1 : 6.69
3	0.157	–	12.01	78.04	90.05	0 : 1 : 3.41	2.50 : 1 : 7.62
4	0.244	0.70	10.02	82.65	93.77	0.28 : 1 : 4.29	2.59 : 1 : 7.97
5	0.484	3.88	7.14	87.38	98.40	2.15 : 1 : 6.39	Not determined

TABLE 3

Precipitant – lithium iodate; acidity of the solution on HNO_3 0.53 N

Experiment No.	Concentration of $LiIO_3$ in the solution (in moles/l)	Found in the precipitate (in %)				Ratio $Li : Zr : IO_3$	Ratio of $K : Zr : IO_3$ with the same molecular concentrations of KIO_3
		Li	Zr	IO_3	Sum		
1	0.049	–	10.27	79.00	89.27	0 : 1 : 4.00	
2	0.092	–	10.45	77.10	87.55	0 : 1 : 3.84	2.08 : 1 : 6.72
3	0.192	–	11.31	75.78	87.09	0 : 1 : 3.51	2.50 : 1 : 7.62*
4	0.287	0.8	8.97	75.88	85.65	0.25 : 1 : 4.45	2.59 : 1 : 7.97**
5	0.490	5.2	7.42	89.22	101.84	2.02 : 1 : 6.25	Not determined

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* With 0.161 N on KIO_3.

** With 0.241 N on KIO_3.

TABLE 4

Precipitating agent – rubidium iodate; acidity of the solution on HNO_3 0.54 N

Experiment No.	Concentration of $RbIO_3$ in the solution (in moles/l)	Found in the precipitate (in %)				Ratio Rb : Zr : IO_3	Ratio of K : Zr : IO_3 with the same molecular concentrations of KIO_3
		Rb	Zr	IO_3	Sum		
1	0.061	13.16	7.01	81.45	101.62	1.99 : 1 : 6.05	1.77 : 1 : 5.65
2	0.078	12.90	6.73	81.50	101.13	2.06 : 1 : 6.31	2.02 : 1 : 5.98
3	0.096	12.96	6.28	82.34	101.58	2.19 : 1 : 6.83	2.08 : 1 : 6.72

It is apparent from a comparison of the data in Tables 1-4 that the composition of the precipitant not only influences the speed of crystallization of the precipitates, but also their final composition.

Upon long standing with a solution of iodic acid (Table 1), zirconium triiodate is converted into the tetraiodate, and not into the hexa- or enaiodate, as with potassium iodate.

Different quantities of the triiodate were converted into the tetraiodate after being allowed to stand for the same length of time (about 1 month) with iodic acid solutions of various concentrations. The reaction goes more completely with low or high concentrations of iodic acid in the solution (Experiments 7, 11, 5, 10 and 15, Table 1). The reasons for the incomplete conversion of the triiodate into the tetraiodate with moderate concentrations of iodic acid in the solution have not been explained.

In a 0.02 N nitric acid solution, with the concentration of iodic acid equal to 0.026 M, the replacement of the hydroxyl groups in the monoiodate by iodate groups is made more difficult as a result of hydrolysis (experiment 1, Table 1). Water of crystallization, as well as hydroxyl groups, made up part of the composition of the hydroxyiodates which were dried in the air; as a result of this the total content of zirconium and of the iodate groups in the precipitate is less than 100%. Two molecules of water of crystallization apparently enter into the composition of zirconium tetraiodate (experiments 5, 10 and 15, Table 1); however, its content in the tetraiodate precipitate has not been definitely determined.

Upon long standing of zirconium triiodate with mother liquors which contain sodium or lithium iodate, the triiodate may be converted into a mixture of the precipitates of the hexa- and enaiodates. The formation of the hexa- and enaiodate takes place only at high concentrations close to saturation with the corresponding iodate (experiment 5, Tables 2 and 3). At lower concentrations of $LiIO_3$ or $NaIO_3$, the behavior of the precipitate is similar to that observed in the experiments with iodic acid. With rubidium, the most stable complex zirconium-iodic acid compounds are formed; therefore, in order to obtain a precipitate of the same concentration as with potassium iodate, a smaller molecular concentration of rubidium iodate in solution is required (Table 4).

On the conversion of hydroxyiodates into complex compounds, the dehydration of the precipitate takes place. According to the analytical data, the total content of the alkali metal, zirconium, and the iodate groups is often somewhat more than 100%; this is probably due to errors in the carrying out of the analysis.

Thus, when the precipitates of zirconium hydroxyiodates are allowed to stand for a long time with solutions containing iodates of the alkali metals, complex compounds of the double salt type of the following composition are formed:

$$Zr(IO_3)_4 \cdot 2MeIO_3 \text{ and } Zr(IO_3)_4 \cdot 3MeIO_3 \cdot 2HIO_3,$$

(Me equals potassium, sodium, lithium, or rubidium).

The stability of the complex iodic acid compounds of zirconium rises with a change in the composition of the precipitant in the following order:

$$LiIO_3,\ NaIO_3,\ KIO_3,\ RbIO_3.$$

With iodic acid, tetraiodates are formed.

2. Reactions in Which Zirconium Hydroxyiodates are Formed.

Many experiments showed that the composition of the precipitate of zirconium iodate depends to a considerable extent on the composition of the zirconium nitrate in solution. Together with this, the concentration of the iodate ion also has an important influence, especially when the precipitation takes place from solutions of increased acidity. The formation of hydroxyiodates is characteristic of zirconium; it is impossible to explain this phenomenon by the properties of zirconium iodate alone. This is graphically illustrated by the results given in Table 5.

When zirconium is precipitated from an aqueous solution of its nitrate (pH 2-3), that is, under conditions of the greatest possible hydrolysis of zirconium nitrate, only the monoiodate appears in the precipitate regardless of the concentration of the iodate ion in the solution (experiment 1, Table 5). The influence of the hydrolysis of zirconium nitrate on the composition of the iodate precipitate is also considerable in a 0.07 N nitric acid solution. On the precipitation of zirconium from such a solution too, the monoiodate is obtained, but in addition, precipitates are also formed which contain more than one iodate group for each zirconium atom (experiments 2,7, and 12, Table 5).

Precipitates which contain one iodate group for each zirconium atom can also be obtained from concentrated nitric acid solutions. In particular, zirconium was isolated in small quantities (in relation to the total content in the solution) in the form of the monoiodate from a 5 N nitric acid solution (experiments 2-5, Table 5).

On the precipitation of zirconium, the gradual formation of the precipitates is observed. This is graphically shown by the results of experiments carried out with 0.5 N and more concentrated nitric acid solutions. With an increase in the concentration of iodate ions in solution, there was an increase not only in the completeness of precipitation, but also in the number of iodate groups in the precipitate in relation to the zirconium content. The final product of the reactions in the solution is zirconium triiodate (experiments 12-15, Table 5).

TABLE 5

Dependence of the composition of zirconium hydroxyiodate on the concentration of iodate ions in solution and the acidity. Concentration of zirconium 0.0076 g-ion/liter

Experiment No.	Concentration of HNO_3 (normality)	Concentration of IO_3 in solution (in g-ion/l)	Ratio of IO_3/Zr in precipitate	Composition of the precipitate
		Zirconium monoiodate		
1	0.02	0.0097-0.161	1.0-1.3	$Zr(OH)_3IO_3 \cdot 4H_2O$
2	0.07	0.008		
3	0.5	0.011		
4	0.99	0.015		
5	5.0	0.037		
		Precipitates containing less than 3 iodate groups		
6	0.02	Not formed	$> 1 < 3$	Variable
7	0.07	0.01-0.14		
8	0.5	0.015-0.06		
9	0.99	0.02-0.06		
10	5.0	0.05-0.06		
		Zirconium triiodate		
11	0.02	Not formed	3.0-3.2	$ZrOH(IO_3)_3 \cdot 4H_2O$
12	0.07	0.152		
13	0.5	0.060-0.3		
14	0.99	0.060-0.35		
15	5.0	0.060-0.57		

The results obtained on fractional precipitation show that zirconium is precipitated when the nitrate groups are fully replaced by iodate groups; therefore, that part of the zirconium which is found in solution in the form of the mononitrate is precipitated, in the first place, in the form of the monoiodate; that part contained in the form of the dinitrate forms the diiodate; and zirconium trinitrate precipitates out in the form of zirconium triiodate.

Considering the process as a reaction between ions, the formation of zirconium hydroxyiodates may be represented by the following scheme:

Monoiodate $Zr(OH)_3^+ + IO_3^- \rightarrow Zr(OH)_3IO_3$.

Diiodate $Zr(OH)_2^{+2} + 2IC_3^- \rightarrow Zr(OH)_2(IO_3)_2$.

Triiodate $ZrOH^{+3} + 3IC_3^- \rightarrow ZrOH(IO_3)_3$.

TABLE 6

Composition of the amorphous and crystalline phases of precipitates isolated before the establishment of equilibrium

Experiment No.	Concentration of HNO_3 (normality)	Ratio of K : Zr : IO_3 according to analysis	
		amorphous	crystalline
1	0.02	0 : 1 : 1.12	1.99 : 1 : 6.04
2		0 : 1 : 1.15	2.02 : 1 : 6.15
3	0.48	0 : 1 : 2.98	2.06 : 1 : 6.17
4		0 : 1 : 3.07	2.06 : 1 : 6.28

TABLE 7

Influence of the relative concentrations of iodic acid and potassium iodate on the composition of the zirconium iodate precipitate

Experiment No.	Concentration of IO_3 (in moles/l)		Numerical value of the ratio of the molecular concentrations of HIO_3 : KIO_3	Numerical value of the ratio IO_3 : Zr in the precipitate.
	total	in KIO_3		
1	0.294	None	–	3.94
2	0.283	0.035	7.10	8.51
3	0.284	0.118	1.40	8.90
4	0.291	0.207	0.41	8.00
5	0.304	0.056	4.40	9.06
6	0.303	0.219	0.38	8.23
7	0.310	0.248	0.25	7.93
8	0.501	None	–	4.11
9	0.437	0.066	5.62	8.23

TABLE 8

Influence of the acidity of the solution on the composition of the zirconium iodate precipitate

Experiment No.	Concentration of HNO_3 (normality)	Concentration of KIO_3 (in moles/l)	Numerical value of the ratio in the precipitate	
			IO_3 : Zr	IO_3 : K
1	0.18	0.094	7.03	3.04
2	0.48	0.095	6.72	3.18
3	0.98	0.091	6.10	2.96
4	1.75	0.099	6.08	2.99
5	3.3	0.094	5.46	5.44
6	4.2	0.090	5.69	4.83
7	0.18	0.156	7.94	3.06
8	0.48	0.161	7.62	3.04
9	0.98	0.167	7.23	3.16
10	1.75	0.155	7.32	3.22
11	3.3	0.168	6.57	3.85
12	4.2	0.156	6.24	3.77

The presence of the $Zr(OH)_3^+$ and $Zr(OH)_2^{+2}$ ions in the nitric acid solutions may be shown by the fractional precipitation of zirconium (at low concentrations of iodate ions in solution). On the addition of a large excess of dissolved iodate to the nitric acid solution, zirconium triiodate is precipitated. If the concentration of iodate ions is increased in a solution from which part of the zirconium has already been precipitated out in the form of the monoiodate or of a mixture with an average content of less than three iodate groups for each zirconium atom, the precipitate is converted into the triiodate.

TABLE 9

The influence of the concentration of the dissolved potassium found in solution on the composition of the zirconium iodate precipitate

Experiment No.	Concentration in the solution (in moles/l)			Numerical value of the ratio in the precipitate		
	HNO_3	IO_3	K	K : Zr	IO_3 : Zr	IO_3 : K
1	3.3	0.133	0.133	1.35	5.89	4.36
2		0.122	0.567	1.85	6.22	3.36
3		0.168	0.168	1.70	6.57	3.87
4		0.160	0.605	2.18	6.71	3.08
5		0.193	0.193	2.03	6.99	3.34
6		0.216	0.681	2.34	7.19	3.07
7	4.2	0.160	0.160	1.65	6.28	3.81
8		0.181	0.626	2.07	6.34	3.06

On the basis of these results, it is evident that the monoiodate and the diiodate, on contact with the mother liquor, can be converted into the triiodate.

Such a conversion can be represented in the following way:

$$Zr(OH)_3IO_3 + 2H^+ + 2IO_3^- \rightarrow ZrOH(IO_3)_3 + 2H_2O,$$

$$Zr(OH)_2(IO_3)_2 + H^+ + IO_3^- \rightarrow ZrOH(IO_3)_3 + H_2O.$$

For 0.5 N and more concentrated nitric acid solutions, the concentration of the iodate ion has more significance than the acidity; therefore, in order to obtain zirconium triiodate, both from 0.5 N and 5 N nitric acid solutions, approximately the same concentration (about 0.06 g-ion/l) of the iodate ion is required (experiments 13-15, Table 5).

The results of a study of the reaction in which zirconium iodate is formed did not confirm the existence of the zirconyl ion in the nitric acid solution. If zirconium were present in the form of the zirconyl ion, zirconyl iodate would probably be formed. This, however, was not observed in any of the experiments carried out with nitric acid solutions of various concentrations (from 0.02 to 7.5 N). In 0.5 N and more concentrated nitric acid solutions, the greater part of the zirconium was found in the form of $ZrOH^{+3}$. In addition, even in a 5 N solution of nitric acid, the $Zr(OH)_3^+$ ion was found, which creates a basis for supposing the existence of the $Zr(OH)_2^{+2}$ ion.

3. Reactions in Which Zirconium Hexa- and Enaiodates are Formed.

The results of the experiments carried out with mixtures of iodic acid and potassium iodate, and with nitric acid solutions containing potassium iodate were used for the examination of these reactions.

The relatively high solubility of potassium iodate in iodic and nitric acid solutions made possible the carrying out of experiments over wide intervals of concentration of the iodate and potassium ions; the comparatively high stability of potassium-zirconium-iodic acid salts made the obtaining of these compounds possible with small concentrations of potassium iodate in solution.

The composition of the precipitates which are formed on the use of potassium iodate on long standing with mother liquors has been examined in detail earlier (2). In the present article this data is supplemented by the results of the analysis of amorphous and crystalline precipitates which separate out before a state of equilibrium had been reached between the solid and liquid phases; data is also given showing the influence of the addition of potassium nitrate on the composition of the precipitates.

The results of the determination of the composition of the amorphous and crystalline phases are given in Table 6. The separation was carried out by the decantation in the mother liquor of the slowly settling amorphous precipitate from the quickly settling crystalline precipitate.

In Table 7 data is given on the composition of zirconium iodate precipitates obtained with changing ratios of the molecular concentrations of iodic acid and potassium iodate, and with a constant concentration of nitric acid in solution equal to 0.02 N. The data of Table 7 show the changes in the quantity of the enaiodate formed with the indicated changes in the composition of the liquid phase.

In Table 8 data is given characterizing the influence of the concentration of nitric acid on the composition of the zirconium iodate precipitate, and in Table 9, the data showing the influence of the concentration of the potassium ion, the concentration of nitric acid remaining constant.

In examining the reaction of the formation of the hexa- and enaiodates, it is necessary to keep in mind that the composition of the final product varies with the nature of the precipitant used. The reaction of the freshly-precipitated hydroxyiodate with the iodic acid contained in the solution is completed with the formation of the tetraiodate. The same final composition is also observed with moderate concentrations of sodium or lithium iodate in the solution.

When the monoiodate is present in the precipitate, three hydroxy groups are replaced by iodate groups. In the hydroxydiiodate, two hydroxy groups are replaced by iodate groups, and in the hydroxytriiodate, one hydroxy group is replaced by an iodate group:

$$Zr(OH)_3IO_3 + 3H^+ + 3IO_3^- \rightarrow Zr(IO_3)_4 + 3H_2O,$$

$$Zr(OH)_2(IO_3)_2 + 2H^+ + 2IO_3^- \rightarrow Zr(IO_3)_4 + 2H_2O,$$

$$Zr(OH)(IO_3)_3 + H^+ + IO_3^- \rightarrow Zr(IO_3)_4 + H_2O.$$

The zirconium tetraiodate which is formed is stable in the presence of iodic acid solutions. When the ions of the alkali metals are present, especially those of potassium and rubidium, the tetraiodate is converted into the hexa- or the enaiodate. If, on the interaction of the precipitate with the solution, the amorphous phase is separated from the crystalline phase, this indicates that the first corresponds in composition to the freshly-precipitated hydroxyiodate, and the second corresponds to the precipitate of the equilibrium phase (Table 6).

The quantity of hexa- and enaiodates which is formed in their mixtures depends on both the total concentration of iodate ions in the solution, and on the ratio of the moelcular concentrations of iodic acid and potassium iodate. With a concentration of iodic acid sufficiently high to prevent the hydrolysis of zirconium iodate, a small concentration of potassium iodate in the solution is necessary for the formation of the hexaiodate. A considerable increase in the concentration of potassium iodate in the solution also does not influence the full conversion of the precipitate into the hexaiodate (Table 7). These, and other experiments show that for the conversion of the triiodate, the relative concentration of iodic acid and potassium iodate is not significant. The only important factors are sufficiently high concentrations of potassium iodate and the hydrogen ion (the raising of the acidity of the solution is necessary to prevent hydrolysis of the zirconium iodate precipitate).

Taking into consideration the conditions of the formation of the hexaiodate, the following scheme is the most reliable representation of its formation:

$$ZrOH(IO_3)_3 + H^+ + IO_3^- + 2KIO_3 \rightarrow Zr(IO_3)_4 \cdot 2KIO_3 + H_2O.$$

For the conversion of the entire precipitate into the enaiodate, the composition of the mother liquor has essential significance. It is necessary that the mother liquor have a high concentration of iodic acid and a relatively low concentration of potassium iodate. With high concentrations of iodic acid and relatively low concentrations of potassium iodate in the solution, the formation of the double salt $KIO_3 \cdot 2HIO_3$ is observed; this salt was studied in detail by Meerburg in 1905 [3].

Starting from the composition of the enaiodate, and from the conditions under which it can be obtained, and taking into consideration the data of the investigation of the system $HIO_3 - KIO_3$ [3], the following scheme is the most probable one for the conversion of the precipitate into the enaiodate:

$$ZrOH(IO_3)_3 + H^+ + IO_3^- + 2KIO_3 + KIO_3 \cdot 2HIO_3 \rightarrow Zr(IO_3)_4 \cdot 3KIO_3 \cdot 2HIO_3 + H_2O.$$

The $KIO_3 \cdot 2HIO_3$ molecules can probably be formed, not only with high concentrations of iodic acid and low concentrations of potassium iodate, but also in these conditions when there is a sufficiently high concentration of the hydrogen, iodate, and potassium ions in the solution. This is evidently the explanation of the ability of zirconium triiodate to form (usually) mixtures of hexaiodate and enaiodate on long standing with the mother liquors.

The formation of the enaiodate takes place, not only on the precipitation of zirconium by a mixture of iodic acid and potassium iodate, but also under those conditions when potassium iodate dissolved in dilute nitric acid or water, is used as a precipitant (with precipitation by potassium iodate dissolved in water, it is necessary to use a nitric acid solution of zirconium nitrate).

When potassium iodate is used, the greatest quantity of the enaiodate is found in the mixture when the mother liquors are saturated with KIO_3; under these conditions, even with an increase in the concentration of the nitric acid, the solubility of the potassium iodate is increased, and the average composition of the mixture of precipitates settling out of 0.18, 0.48, 0.98, 1.75, 4.2, 5.0 and 7.5 N nitric acid solutions turns out to be approximately the same, with the ratio of $Zr : IO_3 = \sim 1 : 8$. With the utilization of a 3.3 N nitric acid solution, saturated with potassium iodate, precipitates with an average content of about 8.6 iodate groups to one zirconium atom were obtained [2]. The last experiment showed that within the limits of 2-4 N nitric acid, saturated with potassium iodate, more favorable conditions are created for the formation of the complex molecules $KIO_3 \cdot 2HIO_3$, than in less concentrated nitric acid solutions.

The high acidity of the solution influences the composition of the precipitates formed with concentrated nitric acid solutions. The formation of acid salts is possible on contact between zirconium iodate and nitric acid solutions; this is disclosed by changes in the numerical value of the ratio between the iodate groups and the potassium in the precipitate. In the normal salts the numerical value of the ratio between the iodate groups and potassium is equal to 3, while in the acid salts it is greater than 3 (Table 9).

Even with the partial replacement of the potassium by the hydrogen ion, the stability of the complex compound is lowered, as a consequence of which the quantity of the enaiodate in the mixture decreases.

With an increase in the concentration of the potassium ion as a result of the introduction of potassium nitrate in a nitric acid solution, the equilibrium is shifted in the direction of the formation of the normal salts; together with this, the quantity of the enaiodate in the precipitate is increased. (experiments 2, 4, 6, and 8, Table 9). The shifting of the equilibrium in the direction indicated is in conformity with the general principle of such changes, since on the addition of potassium nitrate the dissociation of nitric acid is lowered, and the concentration of potassium entering into the composition of the precipitate is increased.

With the use of $LiIO_3$, $NaIO_3$ and $RbIO_3$ as the precipitant, the same conformity with the general principle is observed as in the case of potassium iodate, but when these precipitants are used the individual properties of a given alkali metal also influence the course of the reaction.

SUMMARY

1. The composition of freshly-precipitated zirconium iodate was determined by the extent of the hydrolysis of its nitrate in solution, and also by the concentration of iodate ions.

At a pH of 2-3, zirconium is found in the form of $Zr(OH)_3^+$; therefore, on the addition of the dissolved iodate, the monoiodate is formed. In 0.07 N and more concentrated nitric acid solutions, zirconium forms three types of ions: $Zr(OH)_3^+$, $Zr(OH)_2^{+2}$ and $ZrOH^{+3}$. On the fractional precipitation of zirconium with small portions of the dissolved iodate, the corresponding hydroxyiodates are precipitated:

$$Zr(OH)_3IO_3 \cdot 4H_2O,\ Zr(OH)_2(IO_3)_2 \cdot 4H_2O \text{ and } ZrOH(IO_3)_3 \cdot 4H_2O.$$

Precipitates of two compositions were isolated – the monoiodate and the triiodate. The monoiodate and the diiodate are converted into the triiodate when high concentrations of the iodate ion are present in solution. The zirconyl ion was not detected in the nitric acid solutions.

2. Upon long standing with a mother liquor containing iodic acid, zirconium triiodate is converted into the tetraiodate.

In the presence of the iodates of the alkali metals, the triiodate is converted into the hexa- and the enaiodate.

In solutions of high acidity, the acid salt $Zr(IO_3)_4 \cdot MeIO_3 \cdot HIO_3$, is formed along with the normal salt.

3. The stability of the iodic acid complexes of zirconium compounds increases with the use of precipitants in the following order: $LiIO_3$, $NaIO_3$, KIO_3, $RbIO_3$.

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THE SOLUBILITY PRODUCTS OF THE OXALATES OF SOME RARE-EARTH ELEMENTS AND THE DISSOCIATION CONSTANTS OF THEIR COMPLEX SULFATES

I. M. Korenman

There is very little data in the literature on the solubility products of the oxalates of the rare-earth elements. It is most often mentioned that the solubility product of lanthanum oxalate is equal to $2 \cdot 10^{-28}$ at 18° [1-4]. The value for the solubility product of cerium oxalate according to some data is equal to $2.5 \cdot 10^{-29}$ at 25° [3,4], and for the oxalate of neodymium or praseodymium a value of $5.9 \cdot 10^{-29}$ at 25° is given in [4]. The solubility in water at 25° of the oxalates in which we are interested is given in some works [5]; this data served as the basis for the calculation of the solubility products given above. These results were obtained by the determination of the electroconductivity of saturated solutions. However, according to Semenchenko [6], the method of electroconductivity is not devoid of errors. In addition, the oxalates of the rare-earth elements in their saturated solutions undergo hydrolysis to a certain extent as a consequence of which the results of determinations carried out by this method may be low. Some investigators [7, 8] determine the solubility of the rare-earth elements in sulfuric acid. But the results of the data are insufficient for the calculation of the solubility products; therefore we carried out a series of studies for the determination of the solubility products of the oxalates of lanthanum, cerium and praseodymium. The determination was carried out by the method used by Zharovsky [9] for the determination of the solubility products of phosphates.

We determined the solubility products of oxalates from their solubility in hydrochloric acid solutions of various concentrations. In order to obtain saturated solutions, the oxalate was agitated for three hours with a solution of hydrochloric acid of known concentration. Agitation for this length of time is sufficient to achieve saturation.

$$Me_2(C_2O_4)_3 + 6H^{\cdot} \rightarrow 2Me^{\cdot\cdot\cdot} + 3H_2C_2O_4. \qquad (1)$$

We determined the pH, and the total concentration of the oxalate, s, in the solution obtained in this way; the concentration of the oxalate was determined by titration with permanganate in the presence of manganese sulfate. The concentration of the cation of the rare-earth element was calculated from the value of s that was found:

$$[Me^{\cdot\cdot\cdot}] = \frac{2}{3} s. \qquad (2)$$

The total concentration of oxalic acid was obtained by adding the concentrations of its various forms, which had been titrated with permanganate:

$$s = [C_2O_4''] + [HC_2O_4'] + [H_2C_2O_4]. \qquad (3)$$

The concentration of each form depends on the concentration of the hydrogen ion and on the dissociation constant of oxalic acid

$$[HC_2O_4'] = [C_2O_4''] \cdot \frac{[H^{\cdot}]}{k_2}, \qquad (4)$$

$$[H_2C_2O_4] = [C_2O_4''] \cdot \frac{[H^{\cdot}]^2}{k_1 \cdot k_2}. \qquad (5)$$

Thus, the concentration of HC_2O_4' and $H_2C_2O_4$ can be expressed by the concentration of the C_2O_4'' ion and of the hydrogen ion.

Let us suppose that the total concentration of the oxalate is equal to 1 M; then

$$s = 1 = [C_2O_4''] + [HC_2O_4'] + [H_2C_2O_4]. \qquad (6)$$

We shall substitute for the values of HC_2O_4' and $H_2C_2O_4$ their values from equations (4) and (5):

$$s = 1 = [C_2O_4''] + [C_2O_4''] \cdot \frac{[H^{\cdot}]}{k_2} + [C_2O_4''] \cdot \frac{[H^{\cdot}]^2}{k_1 \cdot k_2}. \qquad (7)$$

whence

$$s = 1 = [C_2O_4^{''}]\left(1 + \frac{[H^{\cdot}]}{k_2} + \frac{[H^{\cdot}]^2}{k_1 \cdot k_2}\right), \tag{8}$$

$$[C_2O_4^{''}] = \frac{k_1 \cdot k_2}{k_1 \cdot k_2 + k_1[H^{\cdot}] + [H^{\cdot}]^2} = \frac{3.96 \cdot 10^{-6}}{3.96 \cdot 10^{-6} + 6.5 \cdot 10^{-2}[H^{\cdot}] + [H^{\cdot}]^2}. \tag{9}$$

Equation (9) makes possible the calculation of the concentration of $C_2O_4^{''}$ in relation to the pH, with s = 1 (Table 1).

TABLE 1

Dependence of the concentration of $C_2O_4^{''}$ on the pH with s = 1

pH	$[C_2O_4^{''}]$	$-\log[C_2O_4^{''}]$
0	$3.7 \cdot 10^{-6}$	5.43
0.5	$3.3 \cdot 10^{-5}$	4.48
1.0	$2.5 \cdot 10^{-4}$	3.60
1.5	$1.3 \cdot 10^{-3}$	2.89
2.0	$6.0 \cdot 10^{-3}$	2.22
2.5	$1.9 \cdot 10^{-2}$	1.72
3.0	$5.7 \cdot 10^{-2}$	1.25
4.0	$3.8 \cdot 10^{-1}$	0.42
5.0	$8.6 \cdot 10^{-1}$	0.07

To simplify calculations, the log $[C_2O_4^{''}]$ is plotted against the pH in accordance with this data. Through the use of such a graph, it is possible easily to find the concentration of $C_2O_4^{''}$ for any value of pH. This concentration of $C_2O_4^{''}$ is multiplied by the value of s found by titration. The product shows the concentration of $C_2O_4^{''}$ in the final solution. Finally, we introduce the values obtained for $C_2O_4^{''}$ and $Me^{\cdot\cdot\cdot}$ in the formula

$$PS = [Me^{\cdot\cdot\cdot}]^2 \cdot [C_2O_4^{''}]^3 \cdot f^2_{Me^{\cdot\cdot\cdot}} \cdot f^3_{C_2O_4^{''}}. \tag{10}$$

We will give an example of the calculations. A saturated solution of lanthanum oxalate in 0.02 N hydrochloric acid was prepared. The concentration of oxalic acid in this solution was $s = 2.25 \cdot 10^{-4}$ M. Therefore, $[La^{\cdot\cdot\cdot}] = 2/3 \cdot 2.55 \cdot 10^{-4} = 1.5 \cdot 10^{-4}$ g-ion/l. The pH of the saturated solution was equal to 1.61. According to the data of Table 1, (or better, from a graph constructed from the data), we find that at this pH the negative logarithm of the concentration of $C_2O_4^{''}$ is equal to 2.7, from which $[C_2O_4^{''}] = 2 \cdot 10^{-3}$ g-ion/l with s = 1. For $s = 2.25 \cdot 10^{-4}$ the concentration of $C_2O_4^{''}$ is equal to:

$$[C_2O_4^{''}] = 2.25 \cdot 10^{-4} \cdot 2 \cdot 10^{-3} = 4.5 \cdot 10^{-7} \text{ g-ion/l.}$$

Since all the determinations were carried out in the presence of comparatively large quantities of an electrolyte (the acid), the activity coefficients of the ions were taken into account in the calculations. The values taken for these coefficients were those given by Lurye [3].

From this data, we will calculate the solubility products of lanthanum oxalate:

$$(1.5 \cdot 10^{-4})^2\,(4.5 \cdot 10^{-7})^3\,(0.42)^2\,(0.68)^3 = 1.07 \cdot 10^{-28}.$$

It is possible to determine the solubility product in a somewhat different way. The concentration of the cation in a saturated solution of the oxalate of the rare-earth element in hydrochloric acid is determined gravimetrically. For this, a known quantity of a saturated solution is evaporated until dry, then evaporated with nitric acid, roasted, and the residue, which is the metal oxide, is weighed. Knowing in this way the concentration of the cation, it is possible to calculate the total concentration of the oxalate, which is 1.5 times greater than the concentration of the cation. On the basis of this data, and the value of the pH of the saturated solution, the concentration of the $C_2O_4^{''}$ ion is found. The further calculations are carried out in the same way as with the preceeding method.

TABLE 2

Determination of the solubility product of calcium oxalate

Run	Normality of HCl	pH of the saturated solution	$[Ca^{\cdot\cdot}]$ (g-ion/l)	$[C_2O_4^{''}]$ (g-ion/l)	f	Activity coefficient
1	0.2	0.92	$9.0 \cdot 10^{-3}$	$1.7 \cdot 10^{-6}$	0.38	$2.2 \cdot 10^{-9}$
2	0.1	1.23	$4.4 \cdot 10^{-3}$	$2.5 \cdot 10^{-6}$	0.45	$1.8 \cdot 10^{-9}$
3	0.2	0.92	$1.1 \cdot 10^{-2}$	$2.2 \cdot 10^{-6}$	0.38	$3.5 \cdot 10^{-9}$
4	0.1	1.23	$5.1 \cdot 10^{-3}$	$2.8 \cdot 10^{-6}$	0.45	$2.3 \cdot 10^{-9}$
					Average	$2.5 \cdot 10^{-9}$

In order to verify the accuracy of the described method for the determination of the solubility products of oxalates, we first determined the solubility product of calcium oxalate at 20°. Calcium oxalate was selected by us because its solubility product has been determined many times and its value is well known. According to various data, this value is between $1.8 \cdot 10^{-9}$ [1-4] and $3.8 \cdot 10^{-9}$ [10]. The results of our determinations• of the solubility product of calcium oxalate are given in Table 2.

The first two determinations were carried out by volumetric methods, the second two – by gravimetric methods.

These results indicate that the method used for the determination of the solubility product (activity coefficient) of oxalates is satisfactorily accurate. The data for the oxalates of lanthanum, cerium, and praseodymium obtained by this method are given in Table 3. Each value is the average of several determinations, which were in good agreement with each other. Thus, our results agree quite well with the literature data. Some of the differences can be explained by differences in temperature and in the methods of the determination of these values.

TABLE 3

Determination of the solubility products of the oxalates of lanthanum, cerium, and praseodymium at 20°

Compound	Normality of HCl	$[Me^{\cdot\cdot\cdot}]$ (g-ion/l)	Total concentration of oxalic acid (in M)	pH of the saturated solution	$[C_2O_4^{''}]$ (g-ion/l)	$f_{C_2O_4^{''}}$	$f_{Me^{\cdot\cdot\cdot}}$	Solubility product	Solubility of the oxalate (in mg/l)
Lanthanum oxalate	0.02	$1.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-4}$	1.61	$4.5 \cdot 10^{-7}$	0.68	0.42	$1.07 \cdot 10^{-28}$	0.54
Cerium oxalate	0.10	$7.7 \cdot 10^{-4}$	$1.15 \cdot 10^{-3}$	1.05	$3.6 \cdot 10^{-7}$	0.46	0.2	$1.10 \cdot 10^{-28}$	0.54
Praseodymium oxalate	0.02	$1.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	1.77	$5.6 \cdot 10^{-7}$	0.68	0.42	$1.3 \cdot 10^{-28}$	0.58

We noticed that the oxalates of the rare-earth elements were considerably more soluble in sulfuric acid than in hydrochloric acid. This can be explained by the fact that in the case of sulfuric acid, the process of solution is accompanied by the formation of complex sulfates. Complex sulfates of the rare-earth elements of various compositions are known. Compounds with the composition $Na_3[Me(SO_4)_3]$ were described many years ago by Brauner [7]. Compounds of the composition $Na[Me(SO_4)_2]$ [5] were also isolated. The $MeSO_4^{\cdot}$ ion [11] is stable in aqueous solutions. Dissociation constants have been determined for several of these ions. The dissociation constant of $LaSO_4^{\cdot}$, found by potentiometric means, is equal to $2.4 \cdot 10^{-4}$ [12]. The dissociation constant of $CeSO_4^{\cdot}$, determined by the ion exchange method, is equal to $1.6 \cdot 10^{-2}$ [13]. The large difference in these values for analogous compounds of two very similar elements indicates that one (or both) of the methods used for the determination was inaccurate.

The increase in the solubility of the oxalates of the rare-earth elements in sulfuric acid compared with their solubility in hydrochloric acid provides a basis for the calculation of the dissociation constants of the complex sulfates of these elements (solubility method). Let us assume that, on dissolution in sulfuric acid, the reaction takes place chiefly according to the following equation:

$$Me_2(C_2O_4)_3 + 6H^{\cdot} + 2SO_4^{''} \rightleftharpoons 2MeSO_4^{\cdot} + 3H_2C_2O_4. \qquad (11)$$

In order to calculate the equilibrium constant, we divide equation (12) by equation (13) raised to the third power and by the square of equation (14):

$$PS = [Me^{\cdot\cdot\cdot}]^2 [C_2O_4^{''}]^3. \qquad (12)$$

$$\frac{[H^{\cdot}]^2 [C_2O_4^{''}]}{[H_2C_2O_4]} = k_1 \cdot k_2. \qquad (13)$$

$$\frac{[Me^{\cdot\cdot\cdot}][SO_4^{''}]}{[MeSO_4^{\cdot}]} = k. \qquad (14)$$

Whence we obtain

$$\frac{[MeSO_4^{\cdot}]^2 [H_2C_2O_4]^3}{[H]^6 [SO_4^{''}]^2} = \frac{PS}{(k_1 \cdot k_2)^3 k^2}. \qquad (15)$$

• E. N. Kuzmina participated in the experimental part of our work.

Equation (15) represents the equilibrium constant of reaction (11). Hence we find that

$$k = \sqrt{\frac{PS\,[H^{\cdot}]^{6}\cdot[SO_4^{''}]^{2}}{(k_1\cdot k_2)^{3}\,(MeSO_4^{'})^{2}\,[H_2C_2O_4]^{3}}}.$$

We now write the equation in simpler form and introduce the activity coefficients for greater accuracy

$$k = \frac{\sqrt{PS}}{7.4\cdot 10^{-5}}\cdot\frac{[H^{\cdot}]^{3}\cdot f_1^{3}\cdot[SO_4^{''}]\cdot f_2}{[MeSO_4^{'}]\cdot f_1\sqrt{[H_2C_2O_4]^{3}}}; \tag{16}$$

in equation (16) f_1 is the activity coefficient of the monovalent ions, and f_2 the activity coefficient of the bivalent ions.

A saturated solution of the oxalate of a rare-earth element in a hydrochloric acid solution of known concentration was prepared. The pH of this solution and the total concentration of the oxalate were determined (titration with permanganate) or the total concentration of the oxalate was determined (gravimetric method). On the basis of this data, the other values necessary for the calculation of the dissociation constant were determined.

1. Knowing the pH of the saturated solution, the value of $[H^{\cdot}]\cdot f_1$ is found by the use of the equation $pH = -\log[H^{\cdot}]\cdot f$.

2. Calculations from the results of the analysis of the saturated solution. 5 ml of a saturated solution of the oxalate of the rare-earth element was titrated using a microburet with a 0.02 N permanganate solution; the total concentration of the oxalic acid was determined from this data. If, on titration, after making deductions for the indicated error, we have 0.68 ml of a 0.02143 N permanganate solution, the total concentration of oxalic acid is equal to:

$$\frac{0.68\cdot 0.02143}{5.2} = 1.46\cdot 10^{-3}\ M$$

It follows from equation (11) that the total concentration of the rare-earth element in the solution is equal to 2/3 of the total concentration of the oxalate. If the total concentration of the rare-earth element in the saturated solution is determined by gravimetric means, the total concentration of the oxalate can be found by multiplying the value for the concentration of the rare-earth element by 3/2.

3. Calculation of the concentration of the undissociated molecules of oxalic acid. For the determination of the dissociation constant through the use of equation (16) it is necessary to know, not the total concentration of the oxalic acid, but the concentration of its undissociated molecules. The total concentration of oxalic acid in the solution, s, is obtained by adding the concentrations of its individual forms (equation 3). Replacing $[HC_2O_4]$ and $[C_2O_4^{''}]$ by their values obtained from the corresponding dissociation constants, we have

$$s = [H_2C_2O_4] + \frac{k_1\,[H_2C_2O_4]}{[H^{\cdot}]} + \frac{k_1\cdot k_2\,[H_2C_2O_4]}{[H^{\cdot}]^{2}},$$

whence

$$s = [H_2C_2O_4]\cdot\left(1 + \frac{5.9\cdot 10^{-2}}{[H^{\cdot}]} + \frac{3.8\cdot 10^{-6}}{[H^{\cdot}]^{2}}\right).$$

If we assume that s = 1, then it is possible to calculate the concentration of the undissociated molecules of oxalic acid in relation to the pH of the solution:

pH	0	0.5	1.0	1.5	2.0	2.5	3.0
$-\log[H_2C_2O_4]$ with s = 1	0.03	0.07	0.20	0.46	0.84	1.30	1.80

In accordance with this data, the $-\log[H_2C_2O_4]$ is plotted against the pH of the solution. For example, when the pH of the solution is equal to 1.35, we find that $-\log[H_2C_2O_4]$ is equal to 0.37 or $\log[H_2C_2O_4] = \bar{1}.63$, whence $[H_2C_2O_4] = 4.27\cdot 10^{-1}$ M, with s = 1. But the total concentration is not equal to 1, but to $1.46\cdot 10^{-3}$ M in our example. Therefore the concentration of the undissociated molecules of oxalic acid is equal to $4.27\cdot 10^{-1}\cdot 1.46\cdot 10^{-3} = 6.2\cdot 10^{-4}$ M.

4. Calculation of the concentration of the complex sulfates. The determination given above gives the total concentration of the rare-earth element in the solution, i.e., the sum of the concentrations of $Me^{\cdot\cdot\cdot}$ and $MeSO_4^{'}$. For our calculations only the concentration of the $MeSO_4^{'}$ ion is required. However, with a sufficiently large concentration of sulfuric acid when the excess of the sulfate ions is many times as great as the total concentration of the

rare-earth element, it is possible to consider that practically the entire concentration of the rare-earth element is found in the form of $MeSO_4^{\cdot}$.

TABLE 4

Determined Dissociation Constants of Complex Sulfate

Exp. No.	Element	Concentration of sulfuric acid	pH	Total concentration		$[H_2C_2O_4]$ (M)	μ	f_1	f_2	Dissociation constant
				oxalic acid	rare-earth element					
1	lanthanum	0.1	1.08	$2.7 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	0.2	0.7	0.40	$5.5 \cdot 10^{-4}$
2		0.1	1.08	$2.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.2	0.7	0.40	$4.7 \cdot 10^{-4}$
3		0.05	1.35	$1.5 \cdot 10^{-3}$	$9.8 \cdot 10^{-4}$	$5.2 \cdot 10^{-4}$	0.1	0.8	0.46	$2.3 \cdot 10^{-4}$
4		0.05	1.35	$1.4 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	0.1	0.8	0.46	$2.9 \cdot 10^{-4}$
5	cerium	0.1	0.96	$1.9 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	0.2	0.7	0.40	$2.1 \cdot 10^{-3}$
6		0.1	0.96	$2.4 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	0.2	0.7	0.40	$1.1 \cdot 10^{-3}$
7		0.05	1.28	$9.8 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	0.1	0.8	0.46	$9.1 \cdot 10^{-4}$
8		0.05	1.28	$1.0 \cdot 10^{-3}$	$6.8 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$	0.1	0.8	0.46	$8.1 \cdot 10^{-4}$
9	praseodymium	0.1	1.04	$1.3 \cdot 10^{-3}$	$9.0 \cdot 10^{-4}$	$7.9 \cdot 10^{-4}$	0.2	0.7	0.40	$3.4 \cdot 10^{-3}$
10		0.1	1.04	$1.2 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$	$7.1 \cdot 10^{-4}$	0.2	0.7	0.40	$4.6 \cdot 10^{-3}$
11	neodymium	0.1	0.99	$2.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	0.2	0.7	0.40	$1.2 \cdot 10^{-3}$
12		0.1	0.99	$1.8 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	0.2	0.7	0.40	$2.0 \cdot 10^{-3}$
13		0.05	1.24	$1.08 \cdot 10^{-3}$	$7.2 \cdot 10^{-4}$	$5.4 \cdot 10^{-4}$	0.1	0.8	0.46	$8.9 \cdot 10^{-4}$
14		0.05	1.24	$1.1 \cdot 10^{-3}$	$7.4 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	0.1	0.8	0.46	$8.5 \cdot 10^{-4}$

In carrying out the calculations, we used the values we had previously obtained for the solubility products of the oxalate of lanthanum, cerium and praseodymium. The solubility product of neodymium oxalate was taken as being equal to the corresponding value for praseodymium. The average results of several determinations are given in Table 4. The odd numbered experiments were carried out by means of volumetric determination of the total concentration, while the even numbered ones were done by gravimetric means.

The following are the average values for the dissociation constants that have been determined: $LaSO_4^{\cdot} = 3.8 \cdot 10^{-4}$, $CeSO_4^{\cdot} = 1.2 \cdot 10^{-3}$, $PrSO_4^{\cdot} = 4.0 \cdot 10^{-3}$, $NdSO_4^{\cdot} = 1.2 \cdot 10^{-3}$.

SUMMARY

1. It has been shown that the determination of the solubility products of slightly soluble oxalates by their solubility in hydrochloric acids gives fully satisfactory results.

2. It has been verified that the solubility products of lanthanum, cerium, and praseodymium are of the order of 10^{-28}.

3. The dissociation constants of the complex sulfates of lanthanum, cerium, praseodymium, and neodymium have been determined; they are of the order of 10^{-3}-10^{-4}.

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STUDY OF THE INTERACTION OF MOLYBDENUM COMPOUNDS WITH SODIUM CHLORIDE

I. INTERACTION OF MoO_3 WITH SODIUM CHLORIDE

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The interaction of molybdenum trioxide with sodium chloride can lead to the formation of sodium molybdate and molybdenum oxychlorides; the exact product depends on the reaction conditions (temperature, the availability of oxygen, and impurities). It is known that in the action of chlorine on MoO_3, the main product is the dioxydichloride MoO_2Cl_2, which is a yellow-white substance, easily sublimable at low temperatures. In accordance with this, the interaction of MoO_3 with sodium chloride in the presence of oxygen can be represented by the reaction:

$$MoO_3 + 2NaCl + 1/2O_2 = Na_2MoO_4 + Cl_2, \qquad (1)$$

$$MoO_3 + Cl_2 = MoO_2Cl_2 + 1/2O_2. \qquad (2)$$

In the absence of oxygen, the mechanism of the reaction may be described in another way: first the formation of the oxychloride and sodium oxide takes place, the latter then enters into a reaction with MoO_3. In this case the evolution of chlorine in general should not take place.

$$MoO_3 + 2NaCl = MoO_2Cl_2 + Na_2O, \qquad (3)$$

$$MoO_3 + Na_2O = Na_2MoO_4, \qquad (4)$$

$$\overline{2MoO_3 + 2NaCl = Na_2MoO_4 + MoO_2Cl_2.} \qquad (5)$$

In accordance with these ideas, the study of the reaction of the interaction of molybdenum trioxide with sodium chloride was carried out both in the air and in an inert gas atmosphere.

The Method of Investigation. A quartz boat containing the investigated substance (weight 3 g) was placed in a quartz tube which was heated by a tubular furnace. Air or an inert gas was drawn through the tube at a fixed rate (about 10 liters/hour). In each experiment we determined the quantity of chlorine evolved, the quantity of molybdenum sublimated, and the quantity of molybdenum leached out of the reaction products which remained in the combustion boat. For the collection of the chlorine, the gases were passed through a system of absorbers containing a potassium iodide solution. The molybdenum oxychloride was sublimated, being condensed in the cold part of the tube, and was carried into solution by means of successive treatment in tubes containing distilled water, dilute hydrochloric acid, and ammonia. The reaction products which remained in the boat were treated with distilled water with agitation for one hour at 85-90°.

The determination of molybdenum in the solutions and in the solid residues was carried out by gravimetric (plumbate) means.

The experiments were carried out at 400, 500, 600 and 700° for one hour.

Chemically pure compounds were used as raw materials; from these, mixtures of the components were prepared which had stoichiometric compositions corresponding to equation (1).

Interaction of Molybdenum Trioxide with Sodium Chloride in an Air Atmosphere.*

The results of this series of experiments are given in Table 1 and on Figures 1 and 2.

The data show that at 400° the speed of the reaction is negligible. Above 400° the speed of the reaction rises sharply: the evolution of chlorine is observed, the cold part of the tube is quickly filled with a goldish crystalline sublimate which becomes yellowish-white upon cooling. Investigation showed that the sublimate was molybdenum dioxydichloride MoO_2Cl_2 (Table 3).

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* With the precipitation of V. Chernyaeva.

It is evident from the data of Table 1 and Figures 1 and 2 that the interaction of molybdenum trioxide with sodium chloride in an air atmosphere takes place with the formation of sodium molybdate and molybdenum oxychloride, and with the evolution of free chlorine. With this, the formation of $NaMoO_4$ and MoO_2Cl_2 can occur both in accordance with reactions (1) and (2) and in accordance with reactions (3) and (4).

Analysis of the curves (Figs. 1 and 2) makes it possible to reach the conclusion that up to 500° the interaction of molybdenum trioxide and sodium chloride leads chiefly to the formation of sodium molybdate (80% of the total quantity of molybdenum). The portion of molybdenum which is sublimated in the form of MoO_2Cl_2 is comparatively small (15% of the total quantity of molybdenum).

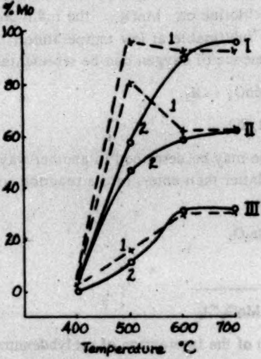


Fig. 1. Dependence of the extent of the formation of MoO_2Cl_2 and Na_2MoO_4 on the temperature for a mixture of MoO_3 and NaCl.
I) Total quantity of reacted molybdenum,
II) molybdenum leached out, III) molybdenum in the sublimates.
1) In an air atmosphere, 2) in an argon atmosphere.

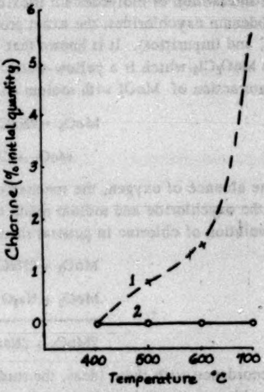


Fig. 2. Dependence of the quantity of chlorine given off on the temperature for mixtures of MoO_3 and NaCl. 1) In air atmosphere, 2) in argon atmosphere.

Since only an insignificant quantity of chlorine is given off at 500°, the formation of Na_2MoO_4 takes place chiefly according to equation (3).

At higher temperatures (600-700°), the quantity of molybdenum increases and the portion of molybdenum combined in the form of Na_2MoO_4 is correspondingly lowered. However, the quantity of chlorine which is given off at 600-700° is considerably larger than at 500°. Therefore, at these temperatures, the portion of MoO_3 reacting with NaCl in accordance with reaction (1) is increased.

It should be pointed out that the total quantity of reacted molybdenum trioxide reaches 93-97% when the reaction has been carried out for one hour in the temperature interval of 500-700°; this indicates the high speed with which the reaction takes place.

Interaction of MoO_3 with Sodium Chloride in an Inert Gas Atmosphere

The experiments were carried out in an atmosphere of argon which had been passed through a tube containing metallic calcium heated to 600° in order to purify it of admixtures of oxygen (0.05%). The results of the experiments are given in Table 2 and in Figs. 1 and 2.

In the absence of oxygen the evolution of chlorine was not observed at any of the investigated temperatures. At 500° and above, large quantities of the sublimates of the oxychloride are formed. The quantity of sublimated molybdenum increases with a rise in temperature and at 600-700° constitutes approximately 30% of the original molybdenum content. The quantity of molybdenum leached out also increases with a rise in temperature and at 600-700° constitutes approximately 60% of the original quantity of molybdenum.

TABLE 1

Interaction of MoO_3 and NaCl in an air atmosphere.
Original weight of charge 3.0 g including 1.12 g of molybdenum

Experiment No.	Temperature	Quantity of chlorine given off		Quantity of molybdenum sublimated		Leaching of the solid residue with water		Total reacted Mo (% of the initial quantity)
		(In g)	In % of the chlorine content in the original charge	(In g)	(In % of the initial quantity)	Mo in solution (in g)	(In % extracted from the original content)	
9	400°	None	None	0.0003	0.027	0.0239	2.13	2.16
10	400	None	None	0.00075	0.067	0.0251	2.24	2.30
11	500	0.00632	0.78	0.1706	15.23	0.8903	79.50	94.73
12	500	0.00747	0.92	0.1781	15.90	0.9289	82.94	98.84
13	600	0.0133	1.64	0.3223	28.77	0.7182	63.94	92.71
14	600	0.0115	1.42	0.3740	33.40	0.6756	60.30	93.70
15	700	0.0468	5.77	0.3523	31.45	0.6609	59.09	90.54
16	700	0.0449	5.54	0.3422	30.55	0.7171	64.02	94.57

TABLE 2

Interaction of MoO_3 with NaCl in an argon atmosphere.
Weight of charge 3.0 g including 1.12 g of molybdenum

Experiment No.	Temperature	Quantity of chlorine given off		Quantity of molybdenum sublimated		Leaching of the solid residue with water		Reacted Mo (in % of the original quantity)
		(In g)	(In % of the chlorine content in the charge)	(In g)	(In % of initial quantity	Molybdenum in solution (in g)	(In % extracted from the original content)	
30	400°	None	None	0.0015	0.13	0.0136	1.21	1.34
31	400	None	None	0.0010	0.09	0.0136	1.21	1.30
32	500	None	None	0.1223	10.92	0.532	47.50	58.42
33	500	None	None	0.1260	11.25	0.507	45.02	56.27
58	600	None	None	0.3427	30.60	0.6766	60.41	91.01
59	600	None	None	0.3530	31.51	0.6326	56.48	87.99
72	700	None	None	0.3305	29.5	–	–	–
73	700	None	None	0.3804	33.96	0.6844	62.00	95.96

TABLE 3

Chemical analysis of the oxychlorides

Temperature of the experiments	Oxychloride obtained in an atmosphere of			
	Air		Argon	
	% Mo	% Cl	% Mo	% Cl
500°	46.5	38.21	45.90	36.96
500	47.56	36.09	46.27	–
600	48.35	37.37	46.40	36.07
600	–	–	46.17	35.14
700	48.38	36.42	47.80	36.93
700	47.38	34.06	48.54	37.52
Average	47.23	36.43	46.85	36.52

The results of the experiments which we carried out confirm the hypothesis expressed above that in the absence of oxygen the interaction of molybdenum trioxide with sodium chloride takes place in accordance with equations (3) and (4); together with this, one would expect that the oxychloride and the sodium molybdate formed in accordance with equations (3) and (4) would each contain the same portions of the original quantity of molybdenum. However, the quantity of molybdenum linked in the form of Na_2MoO_4, is considerably larger than that combined in the form of MoO_2Cl_2. This is explained by the fact that sodium molybdate reacts with molybdenum trioxide, forming polymolybdates, e.g. $Na_2O \cdot 2MoO_3$, $Na_2O \cdot 4MoO_3$ (Fig. 3), which leads to an increase in the proportion of molybdenum which is leached out.

STRONTIUM METANIOBATE AND ITS HYDRATES

E. I. Krylov and Yu. I. Alekseev

According to Larsson's data [1], strontium niobate is precipitated from potassium niobate solutions by strontium salts. By the recrystallization of this precipitate from molten boric acid, comparatively well-formed crystals of strontium niobate are obtained. Chemical analysis of these crystals showed a higher content of Nb_2O_5 than corresponds to any of the theoretically possible formulas that have been established for this compound.

Pierre Süe [2] investigated the interaction of solutions of $Na_{14}Nb_{12}O_{37}$ with solutions of strontium salts. The measurement of the electroconductivity of mixtures of these solutions indicates formation of strontium niobate with the ratio of the basic oxide to the acid equal to 7:6. However, this salt was not obtained in a pure form, since it always contained admixtures of strontium hydroxide.

Other writers have studied the interaction of strontium oxide or its carbonate with niobium pentoxide at high temperatures; the compounds $SrO \cdot Nb_2O_5$ and $4SrO \cdot Nb_2O_5$ were obtained in these experiments [3].

The aim of the present work was to study the conditions of obtaining the properties of strontium metaniobate and its hydrates.

Initial Materials

The niobium pentoxide which was used in this work contained 99.7% Nb_2O_5 and 0.3% TiO_2; we therefore undertook its further purification from titanium through the use of salicyclic acid [4]. The compound Nb_2O_5 which had been purified in this way showed a negative reaction for titanium with hydrogen peroxide.

Strontium hydroxide $Sr(OH)_2 \cdot 8H_2O$ was prepared by Karyakin's method [5], by precipitation from a saturated aqueous strontium nitrate solution with 25% KOH. The radioactive isotope of strontium Sr^{89} with a half-life of 54.5 days was also utilized in our work.

The potassium metaniobate $KNbO_3$ which was required for the synthesis of strontium metaniobate was prepared by the fusion of equimolecular quantities of potassium carbonate and niobium pentoxide according to the method worked out by Lapitsky [6].

Methods of Analysis

The quantity of water of crystallization was determined by the difference in weight after dehydration at 500°C of a sample of strontium metaniobate which had been previously dried to constant weight at 100°.

For the determination of niobium pentoxide, a weighed portion of strontium metaniobate (which had been dried at 100°) was dissolved in concentrated HNO_3, which contained an admixture of H_2O_2. The solution was neutralized with ammonia to pH 6.2, diluted with water to 100 ml and boiled; thereupon, niobic acid was precipitated from the solution, which contained strontium; the precipitate was then filtered and washed. After drying, the filter and the precipitate containing Nb_2O_5 were roasted in a porcelain crucible to constant weight.

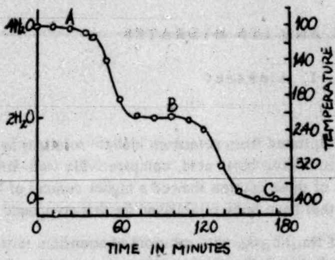
Strontium was determined in the filtrate and in the wash water in the form of strontium sulfate by the usual method [7], after the precipitation of niobic acid.

EXPERIMENTAL

1. The obtaining of the crystal hydrate of strontium metaniobate. No method of preparing the crystal hydrates of strontium metaniobate is mentioned in the literature.

Neither Larsson [1] nor Pierre Süe [2] succeeded in obtaining a pure product. In view of the fact that the precipitation of strontium metaniobate takes place from strongly akaline solutions with pH > 8.9, we used a strontium hydroxide solution which was saturated at room temperature for its preparation, and not the soluble strontium salts. In this way the precipitation of strontium hydroxide along with strontium metaniobate was avoided.

Strontium metaniobate was precipitated by the addition of the corresponding volume of a standard solution (0.048 g/ml Sr^{++}) to the calculated quantity of potassium metaniobate, dissolved in a 1 N solution of KOH.



Hydrates of strontium metamobates.
A) $Sr(NbO_3)_2 \cdot 4H_2O$, B) $Sr(NbO_3)_2 \cdot 2H_2O$, C) $Sr(NbO_3)_2$.

The solution of strontium hydroxide was prepared separately for each test with the observation of the necessary precautions, since it absorbs carbon dioxide from the air very quickly. The strontium metaniobate precipitate was filtered, carefully washed, and dried at 100°.

The obtained salt was analyzed. Weight of sample 0.1339 g.

Found %: Nb_2O_5 61.1; SrO 23.59; H_2O 16.31. $Sr(NbO_3)_2 \cdot 4H_2O$. Calculated %: Nb_2O_5 60.18; SrO 23.53; H_2O 16.29.

It follows from the analysis that the substance prepared by us was strontium metaniobate, containing four molecules of water of crystallization.

2. Dehydration of $Sr(NbO_3)_2 \cdot 4H_2O$. In order to determine the composition and number of intermediate crystal hydrates of strontium metaniobate, we studied its dehydration with a continuous rise in temperature. This method, as was shown by Guichard [8], makes possible the establishment of the nature of the chemical bond between the molecules of water and the solid substance, i.e., it enables us to determine whether it is a hydrated bond or is maintained as a result of the action of special forces (adsorption forces) on the surface of the solid body. In the first case the system will be monovariant, in the second – divariant. Experiments on the dehydration of hydrates with rising temperatures require the simultaneous measurement of the weight of the substance and the temperature for each moment of time. This is accomplished through the use of spring microbalances of the type used by McBain and Bakr [9]. The loss of weight of the crystal hydrate sample, caused by its dissociation with a rise in temperature, is recorded by a microcathetometer. The temperature was measured with a mercury thermometer over a range of 500° with an accuracy of up to ± 2°.

The curve showing the dependence of the change of weight of $Sr(NbO_3)_2 \cdot 4H_2O$, with a continuously rising temperature, on time is given in the figure.

From the analysis of this curve it follows that the first horizontal section A, corresponds to the tetrahydate, which, judging by the slope of the curve, begins to dissociate to a considerable degree at 110° with the formation of a hydrate containing a smaller quantity of water of crystallization. The second horizontal section, B, corresponds in its composition to the dihydrate of strontium metaniobate. This compound, under the conditions of the experiment, was stable within the temperature range from 210 to 260°. Above 260° the dihydrate begins to dissociate, and at 390° it has almost completely decomposed with the formation of anhydrous strontium metaniobate (section C).

3. The solubility of $Sr(NbO_3)_2 \cdot 4H_2O$ was determined by radiometric means. A radioactive compound $Sr(NbO_3)_2 \cdot 4H_2O$, was prepared; it contained, along with ordinary strontium, the radioactive isotope of strontium Sr^{89}. The original preparation according to its β-radiation had an activity of 1054 pulses per minute for 1 mg of $Sr(NbO_3)_2 \cdot 4H_2O$. The measurements were made with a cylindrical β-counter on a calculating apparatus of the "B" type.

In order to determine the solubility, a weighed portion of about 0.5 g $Sr(NbO_3)_2 \cdot 4H_2O$ was introduced into a vessel (equipped with a stirrer) containing 200 ml of twice-distilled water. This vessel and its contents were kept for not less than 24 hours, with constant stirring, in an ultrathermostat in which the temperature was maintained at a constant level within ± 0.2°. The equilibrium was considered achieved when two samples of 15 ml each of a solution, filtered through an ultrafilter, taken eight hours apart, showed corresponding results on the β-counter (about 75 ± 4 pulses per minute). Simultaneously, the activity of a standard solution, prepared by the dissolution of 0.1554 g $Sr(NbO_3)_2 \cdot 4H_2O$ in 200 ml of concentrated nitric acid containing a small quantity of hydrogen peroxide was measured.

The determination of the solubility of $Sr(NbO_3)_2 \cdot 4H_2O$ was carried out at 15, 25 and 50°. The results are given in Table 1.

4. X-Ray Examination.* Structure of the Tetrahydrate of Strontium Metaniobate.

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* With the participation of A. K. Shtolts.

TABLE 1

Solubility of $Sr(NbO_3)_2 \cdot 4H_2O$ in water

Temperature	Solubility	
	(In g/l)	(In M)
15°	0.00607	$1.4 \cdot 10^{-5}$
25	0.01032	$2.33 \cdot 10^{-4}$
50	0.01205	$2.72 \cdot 10^{-4}$

The compound was studied by the powder method. An X-ray photograph was produced using copper radiation in a camera with the radius of the cylindrical adapter R = 28.73 mm. The position of the lines on the X-ray photograph were determined with an accuracy of up to 0.2 mm. The intensity of the lines was evaluated visually.

TABLE 2

Magnitude of the interplanar distances of the crystals $Sr(NbO_3)_2 \cdot 4H_2O$

Line Number	Intensity (I)	Distance (d)	Line Number	Intensity (I)	Distance (d)
1	Strong	3.50	12	Weak	1.443
2	Average	3.03	13	Average	1.415
3	Average	2.83	14	Weak	1.286
4	Strong	2.45	15	Weak	1.185
5	Average	2.27	16	Average	1.157
6	Average	2.13	17	Weak	1.073
7	Strong	2.03	18	Weak	1.057
8	Strong	1.91	19	Weak	0.966
9	Weak	1.81	20	Weak	0.896
10	Weak	1.73	21	Weak	0.882
11	Weak	1.55			

The results of the determination of the interplanar distances in $Sr(NbO_3)_2 \cdot 4H_2O$ crystals and the intensity of the corresponding lines on the X-ray photograph are given in Table 2.

The hypothesis was expressed that the structure of this compound is similar to that of strontium nitrate in which the nitrogen atoms have been replaced by niobium atoms. The strontium atoms form a face-centered cubic lattice. The niobium ions are located in this lattice, but not in the centers of the eight octants; they are, rather, considerably askew. The $[NbO_3]^{1-}$ ions have the form of a triangle. The elementary cell, formed by the strontium ions, thus contains 4 strontium ions, 8 niobium ions, and 24 oxygen ions. In addition, 16 molecules of water enter into the composition of the cell.

The parameter of the lattice, a, calculated according to all the lines of the crystallogram, is equal to 8.56A.

Assuming the structure indicated above for the compound, and using the parameter of the lattice calculated from the crystallogram, it is possible to determine the density of the compound according to the formula

$$\delta = \frac{nA_{av.}\ 1.65 \cdot 10^{-24}}{Q},$$

where n is the number of ions in the elementary cell, $A_{av.}$ – the average atomic weight, and Q – the volume of the elementary cell.

The density of $Sr(NbO_3)_2 \cdot 4H_2O$, calculated in this way, is equal to 4.64 g/cm³.

The density of this compound, determined with a pyknometer, is 4.663 g/cm³ ; this confirms our hypothesis on the structure of $Sr(NbO_3)_2 \cdot 4H_2O$.

5. The melting point of anhydrous strontium metaniobate was determined from cooling and heating curves, using platinum-platinum and rhodium thermocouples. The thermocouples were calibrated from the melting points of the chemically pure salts KNO_3, KCl, Na_2SO_4 and K_2SO_4.

The melting point of anhydrous strontium metaniobate proved to be 1225 ± 20°.

SUMMARY

1. Strontium metaniobate and its tetrahydrate $Sr(NbO_3)_2 \cdot 4H_2O$ have been prepared.

2. The dihydrate of strontium metaniobate, $Sr(NbO_3)_2 \cdot 2H_2O$, has been detected by the method of dehydration with a continuous rise in temperature.

3. The solubility of $Sr(NbO_3)_2 \cdot 4H_2O$ at 15, 25 and 50° has been studied by radioactive means.

4. The parameter of the crystal lattice of $Sr(NbO_3)_2 \cdot 4H_2O$ has been determined; the value of the density of the compounds, obtained from this data, has been found to be in satisfactory agreement with that determined by pyknometric means.

5. The melting point of strontium metaniobate has been determined; it is 1225 ± 20°.

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* T. p. = C. B. Translation pagination.

THE ENTHALPY OF FORMATION OF LITHIUM STIBIDE

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Lithium stibide is formed on the direct interaction of the simple substances at high temperatures, or by the action of antimony on a solution of lithium in liquid ammonia.

We prepared lithium stibide by melting lithium and antimony, taken in stoichiometric proportions, in hermetically sealed steel crucibles. The melting was carried out over the course of several hours with frequent stirring and temperatures up to 1250°.

The X-ray photograph of the preparation obtained in this way showed the absence of free antimony; the interplanar distances found by us coincided with those obtained by Zintl [1]. It also turned out that on fusion no significant amount of iron, or other component of steel, was introduced in the preparation. The contents of lithium and antimony in the preparation were very close to those corresponding to the formula Li_3Sb. All the operations with lithium stibide were carried out in an atmosphere of dry carbon dioxide.

The enthalpy of formation was determined on the basis of the value for the enthalpy of solution of the stibide in dilute hydrochloric acid.

It had been established in preliminary experiments that about 1-2% of the antimony forms stibine under these conditions; since the enthalpy of formation of stibine is of a fairly large magnitude, this could introduce an important error in the determination of the heat of formation of Li_3Sb.

In order to exclude this possibility, we used in our calorimetric experiments, not a pure hydrochloric acid solution, but one which contained lithium stibide; the presence of finely-crushed antimony in the solution, as was shown by specially conducted experiments, reduces the quantity of stibine formed to practically zero.

The enthalpy of the reaction of the dissolution of Li_3Sb in hydrochloric acid was measured in an adiabatic calorimeter. An ampoule containing a weighed portion of the preparation was placed in a glass, hermetically sealed chamber into which was poured about 40 ml of hydrochloric acid (0.9 N). At the same time, the ampoule was broken with a glass spatula, which also served as a stirrer. The chamber was placed in a calorimetric vessel — a brass beaker with a capacity of about 2 liters, equipped with a stirrer. 1500 g of water was poured into this vessel.

The hydrogen which was formed in the process of solution was run through a glass coil, which guaranteed the possibility of heat exchange with the calorimeter.

The change in temperature of the calorimeter was established from the change in resistance (which was measured with a Wheatstone bridge with an accuracy up to 0.1Ω. Since a change in temperature of 1° corresponded to a change in resistance of 705 Ω, this made possible the measurement of the temperature with an accurady of up to ~0.00015°.

The calorimetric vessel was placed in a brass jacket, which was in turn immersed in a vat of water, the temperature of which was kept constant at 25 ± 0.005°. The thermal capacity of the calorimeter was determined from the value of the enthalpy of solution of magnesium which had been prepared by vacuum distillation; it was 2.788 ± 0.017 cal /Ω. For the enthalpy of the process

$$Li_3Sb_{cr} + 3HCl_{s\text{-}s} = 3LiCl_{s\text{-}s} + 3/2H_2$$

(concentration of hydrochloric acid: 1 mole HCl to 80 moles H_2O) in three successive experiments, conducted with different preparations, the following values were obtained: −121.8, −123.0, −126.6 kcal/mole Li_3Sb. In conjunction with the enthalpies of formation of HCl and LiCl and the enthalpies of their solutions (corresponding to the concentrations of their solutions present in our calorimetric experiments) this gives for an enthalpy of formation of Li_3Sb −78.4, −77.2, and −73.7 kcal/mole.

The crystallogram of the preparation for which the enthalpy of formation was found to be equal to −73.7 kcal/mole, showed very weak lines for antimony. The first two values, on the other hand, were obtained for preparations for which the crystallograms showed no antimony lines. This gave us a basis for taking the average of the first two values, i.e., for proposing a value of −77.8 kcal/mole, for the enthalpy of formation of lithium stibide.

$$3Li_{cr} + Sb_{cr} = Li_3Sb + 77.8 \text{ kcal at } 25°.$$

A value of −55.0 kcal/mole was obtained for the enthalpy of formation of lithium bismuthide by Kubaschewski and Seitz [2]. Thus, in going from the antimonous compounds of lithium to the bismuthous compounds, a considerable lowering of the enthalpy of formation takes place. The same phenomenon is also observed for compounds of these elements with magnesium.

SUMMARY

The enthalpy of formation of lithium stibide at 25°, has been determined; it is equal to −77.8 kcal/mole.

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THE THERMAL STABILITY OF COPPER HALIDES

S. A. Shchukarev and M. A. Oranskaya

Copper, on interaction with halides, gives two types of compounds, $CuHal_2$, and CuHal.

CuF_2, $CuCl_2$, $CuBr_2$,

CuF, CuCl, CuBr, CuI.

The compound which is the most stable thermally of the above copper halides is CuF_2. According to Watenberg [1], CuF_2 undergoes considerable dissociation only at temperatures above 600-700°C.

$$CuF_2 + 79.4 \text{ kcal} = CuF + \frac{1}{2} F_2.$$

$CuCl_2$ is decomposed at lower temperature (Proust [2]). Ephraim [3], Tarasenkov, Grigorovich and Boroslovskaya [4], heating $CuCl_2$ in a vacuum, determined its dissociation pressure directly. Jellinek and Koop [5] calculated the dissociation pressure of $CuCl_2$ on the basis of the equilibrium constants which they determined for the reduction of $CuCl_2$ by hydrogen at 251, 325 and 397°. The values calculated by Jellinek do not coincide with those obtained by direct methods by Ephraim and by Tarasenkov and co-workers (Fig. 1).

There is no data on the dissociation pressure of $CuBr_2$ in the literature. CuI_2 has not been obtained in solid form, although Fedotyev [6] observed Cu^{++} ions in aqueous solution on the action of an excess of iodine on suspended CuI.

Unlike CuF_2, CuF is thermodynamically unstable even at room temperature; the reaction of its disproportionnation is exothermic

$$2CuF - 29.4 \text{ kcal} = CuF_2 + Cu.$$

The fact that, on the reduction of CuF_2 with hydrogen, Jellinek and Rudat [7] always obtained metallic copper and not CuF, also indicates the instability of CuF. In contrast to copper fluoride, CuCl, CuBr and CuI are not inclined to disproportionation, and are decomposed thermally into the metal and the halogen only at very high temperatures. Copper chloride is the compound in this group which has been most throughly studied.

A great deal of work has been done on the reduction of copper chloride. One of the first workers in this field was Ribalkin [8], who reduced CuCl with hydrogen in sealed ampoules at 200-400°. Ribalkin did not determine the pressure in the ampoules and therefore his values are not comparable with those of other authors; but the great value of the work of Ribalkin consists in the fact that he was one of the few who studied the equilibrium of CuCl with hydrogen, both from the direction of the reaction of the reduction of CuCl with hydrogen, and from the direction of the oxidation of copper with hydrogen chloride. In addition, the equilibrium of the reduction of copper chloride was studied by Jellinek and Uloth [9], Parravano and Malquori [10], Watanabe [11], Kapustinsky [12], and Partington and Towndrow [13]. This reaction was studied over the widest temperature range by Watanabe. As is evident from Fig. 3, the data of Jellinek and that of Partington and Towndrow do not agree with that of the other authors.

The equilibria of the reduction of copper bromide and copper iodide with hydrogen were studied by Jellinek and his students Uloth [14] and Rudat [15]. The reduction of copper iodide with hydrogen was studied by them at 675-1100°C; at these temperatures, the dissociation of hydrogen iodide is of quite a large magnitude, but they did not take this circumstance into account in the calculation of the equilibrium constants; consequently, there is some doubt of the accuracy of their results.

In the present work, we have determined the dissociation pressure for copper (I) and copper (II) chloride, and for copper (I) and copper (II) bromide.

EXPERIMENTAL

Kahlbaum brand "for analysis" quality $CuCl_2$ and $CuBr_2$ were used, being dehydrated before the experiments: $CuCl_2$ – by heating in a stream of hydrogen chloride (~150°), $CuBr_2$ – in a desiccator over phosphoric anhydride.

THE THERMAL STABILITY OF COPPER HALIDES

A. Chubarov and M. A. Orekhova

Copper, on interaction with halides, gives two types of compounds, $CuHal_2$ and CuHal:

CuF_2, $CuCl_2$, $CuBr_2$,

CuF, CuCl, CuBr, CuI.

The compound which is the most stable thermally of the above copper halides is CuF_2. According to Wartenberg [1], CuF_2 undergoes considerable dissociation only at temperatures above 900-1000°:

$$CuF_2 + 79.4\ kcal = CuF + \frac{1}{2}F_2.$$

$CuCl_2$ is decomposed at lower temperatures ([illegible] [2], Epshtein [3], Tsetsadze, Chigvintsev and Smirnovskaya [4], heating $CuCl_2$ in a vacuum, determined its dissociation pressure directly. Jellinek and Kopp [5] calculated the dissociation pressure of $CuCl_2$ on the basis of the equilibrium constants which they determined for the reduction of $CuCl_2$ by hydrogen at 361, 395 and 455°. The values calculated by Jellinek do not coincide with those obtained by direct methods by Epshtein and by Tsetsadze and co-workers (Fig. 1).

There is no data on the dissociation pressure of $CuBr_2$ in the literature. CuI_2 has not been obtained in solid form, although Fedorov [6] observed Cu^{++} ions in aqueous solution on the action of an excess of iodine on suspended CuI.

Unlike CuF_2, CuF is thermodynamically unstable even at room temperature; the reaction of its disproportionation is exothermic:

$$2CuF - 38.5\ kcal = CuF_2 + Cu.$$

The fact that on the reduction of CuF_2 with hydrogen, Jellinek and Rudat [7] always obtained metallic copper and not CuF, also indicates the instability of CuF. In contrast to copper fluoride, CuCl, CuBr and CuI are not inclined to disproportionation, and are decomposed thermally into the metal and the halogen only at very high temperatures. Copper chloride is the compound in this group which has been most thoroughly studied.

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In the present work, we have determined the dissociation pressure for copper (I) and copper (II) chloride, and for copper (I) and copper (II) bromide.

EXPERIMENTAL

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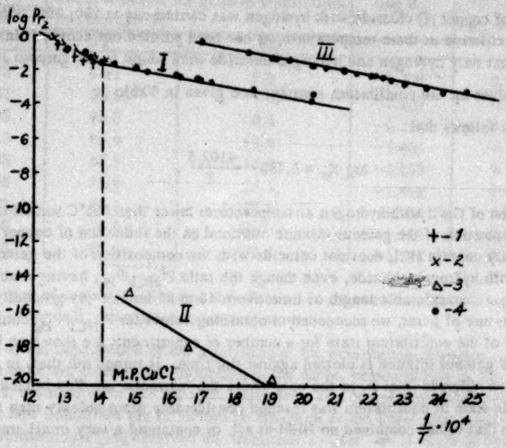

Fig. 1. Dependence of the logarithm of the dissociation pressure of copper (II) chloride and copper (II) bromide on 1/T.
I) $CuCl_2$, II) $CuCl_2$, III) $CuBr_2$.
1) Ephraim's data [3], 2) Tarasenkov's data [4], 3) Data of Jellinek and Koop [5], 4) Our data.

TABLE 3

Temperature		Composition of the equilibrium mixture (in %)		log K_e	$K_e = \frac{P^2_{HCl}}{P_{H_2}}$	Experimental error
°C	°K	H_2	HCl			
250	523	93.6	6.4	−2.337	0.0045	± 0.0005
300	573	80.85	19.15	−1.315	0.048	± 0.002
325	598	75.9	24.1	−1.071	0.085	± 0.003
350	623	68.1	31.9	−0.796	0.16	± 0.01

The vapor pressure of CuBr (Stell [17]) reaches 1 mm at 572°C.

The value for the dissociation pressure of $CuCl_2$ obtained by us, as is evident from Fig. 1, agrees with the data obtained by Ephraim and by Tarasenkov and co-workers as far as the order of magnitude is concerned. The values for the dissociation pressure calculated by Jellinek are of an entirely different order than those of the other authors (curve II, Fig. 1).

Determination of the dissociation pressure of copper (I) chloride and copper (I) bromide. Copper (I) chloride and copper (I) bromide are not decomposed to any significant extent even on heating to 800-900°C in a vacuum; it was therefore necessary to determine the dissociation pressures of these compounds indirectly by the determination of the equilibrium of some reaction in which the investigated substance takes part. We chose the reaction of the reduction of the halides with hydrogen. The method of the investigation was that of circulation. Equilibrium was approached from both directions (CuHal + H_2 and Cu + 2HHal). An excess of HHal was obtained by first heating the investigated substance in an atmosphere of hydrogen to 50-100° above the investigated temperature and then quickly cooling it to the temperature of the experiment. The pressure of the system was held constant during the experiment at 30-40 mm above atmospheric pressure. The partial pressures of the hydrogen and the hydrogen halide entering into the equation of the equilibrium constant of the reaction $K_e = P^2_{HHal}/P_{H_2}$, were calculated on the basis of the analysis of the gaseous reaction products. Further, by combining this equilibrium constant with the equilibrium constant of the reaction of formation of the hydrogen halide, it is possible to calculate the dissociation pressure of the salt.

The reduction of copper (I) chloride with hydrogen was carried out at 250, 300, 325 and 350°C. The vapor pressure of copper (I) chloride at these temperatures, as has been pointed out above, is insignificant; it is therefore possible to consider that only hydrogen and hydrogen chloride were found in the gaseous state.

The average values for the equilibrium constants are given in Table 3.

From Table 3 it follows that

$$\log K_e = 5.789 - \frac{4102.6}{T}.$$

On the reduction of CuCl with hydrogen at temperatures lower than 325°C something like a false equilibrium is observed. The composition of the gaseous mixture obtained on the reduction of copper (I) chloride with hydrogen, which did not originally contain HCl, does not coincide with the composition of the gaseous mixture obtained on the oxidation of copper with hydrogen chloride, even though the ratio P^2_{HCl}/P_{H_2}, having reached a certain value, remained constant for a considerable length of time (from 10 to 20 hours). By gradually changing the original composition of the mixture of gases, we succeeded in obtaining values for P^2_{HCl}/P_{H_2} converging from both directions. Approximations of the equilibrium state for a number of experiments are shown on Fig. 2, where the change in the composition of the gaseous mixture is plotted against the time. It turned out that, in the case of the interaction of copper with hydrogen chloride (that is, in the case where the substance was first heated above the temperature of the experiment), the state of equilibrium was reached considerably more quickly than in the case when copper was reacted with hydrogen that either contained no HHal at all, or contained a very small amount of it.

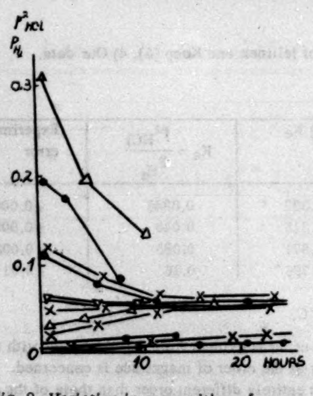

Fig. 2. Variation in composition of gaseous mixture upon approaching equilibrium at 300°C for the reaction $2CuCl + H_2 \rightleftharpoons 2Cu + 2HCl$.

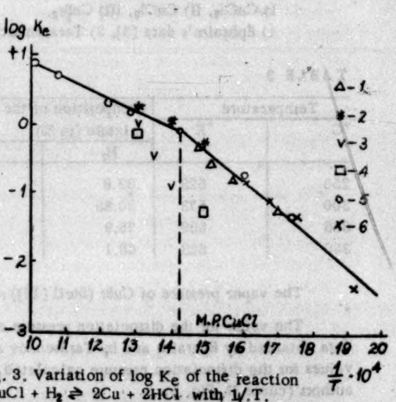

Fig. 3. Variation of log K_e of the reaction $2CuCl + H_2 \rightleftharpoons 2Cu + 2HCl$ with 1/T.
1) Kapustinsky [12]; 2) Parravano and Maliquori [10]; 3) Jellinek [9]; 4) Partington and Towndrow [13]; 5) Watanabe [11]; 6) our data.

The reduction of copper (I) bromide with hydrogen was carried out at 300, 315, 325, 340, 350, 375, 400, 480 and 550°C.

The average values obtained for the equilibrium constants of the reaction are given in Table 4.

From the data of Table 4, the log K_e can be determined.

$$\log K_e = 7.037 - \frac{5491.0}{T} \text{ from 300-350°C.}$$

TABLE 4

Temperature		Composition of the gaseous equilibrium mixture (in %)		log K_e	$K_e = \frac{P^2_{HBr}}{P_{H_2}}$	Experimental error
°C	°K	H_2	HBr			
300	573	94.1	5.9	−2.420	0.0038	±0.0002
315	588	92.55	7.45	−2.201	0.0063	±0.0007
325	598	90.6	9.4	−2.000	0.010	±0.001
340	613	89.0	11.0	−1.820	0.015	–
350	623	86.9	13.2	−1.658	0.022	±0.001
375	648	85.9	14.1	−1.620	0.024	–
400	673	83.1	16.9	−1.432	0.037	±0.002
480	753	79.0	21.0	−1.222	0.060	–
550	823	68.6	31.4	−0.796	0.16	±0.01

Just as in the case of copper (I) chloride, the reaction of the reduction of CuBr below 325°C without the preliminary heating of the salt takes place extremely slowly.

In Figs. 3 and 4, the dependence of the logarithms of the equilibrium constants on 1/T is plotted., While for copper (I) chloride, there is one inflection in the curve, corresponding to the melting point of CuCl, in the case of copper (I) bromide there are two such inflections: at a temperature above 350°, and at 480°C. Copper (I) bromide melts at 480°; therefore the inflection in the curve at the lower temperature corresponds to some change in the solid state. Monkemeyer [18] observed the transition α-CuBr $\rightleftharpoons$ β-CuBr at 384°C, Krug and Sieg [19] determined the presence of three crystalline modifications of copper (I) bromide: γ-CuBr exists below 390°, β-exists from 391-470°, and α- exists from 470-488°; therefore, the inflection from 350-480° corresponds to a double change in the crystal lattice of copper (I) bromide.

As is evident from Figs. 1 and 3, the data obtained by Jellinek for $CuCl_2$ and CuCl is considerably different (often by several orders) from the data of the other authors. The same is true in the case of CuBr. The values obtained by us are considerably higher than those obtained by Jellinek at the same temperature (Fig. 4). The same is also true for a number of other compounds ($CrCl_3$, and $CrCl_2$ etc); in all these cases the values obtained by Jellinek were lower than those of the other authors. This circumstance can only be explained by defects in Jellinek's basic method. The essence of the method used by him for the study of heterogeneous equilibria (for example, of reduction) can be recalled briefly. A gas – the reducer – was passed at a specific rate of speed over the substance, which was in a furnace kept at a constant temperature. The compositions of the mixture of gases were determined for 2-3 different rates, and the values obtained were plotted on a graph: the rate of the reducing gas against the composition of the gaseous mixture; the curve so obtained was extrapolated to a value of zero for the rate of the gas. This extrapolated composition of the gaseous mixture was taken as the equilibrium composition.

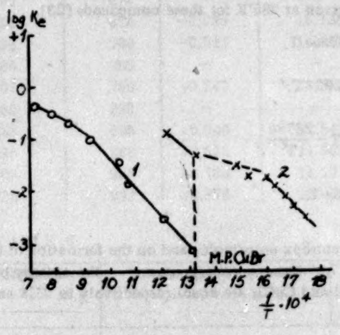

Fig. 4. Variation of log K_e of the reaction $2CuBr + H_2 \rightleftharpoons 2Cu + 2HBr$ with 1/T. 1) Jellinek's data [14]; 2) our data.

In addition to the difficulty of extrapolation from the observation of scattered points [20], there are also difficulties of a basic character• : at low temperatures the rate of flow of the gas, no matter how slow it may be, may be incomparably larger than the speed of the establishment of the equilibrium. In this case, the gases coming out of the furnace will be very far from the equilibrium composition, and the extrapolation can give low

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• Jellinek himself determined the compositions of the mixture of gases at not more than three gas rates.

values. At higher temperatures, on the other hand, the speed of the establishment of the equilibrium can be incomparably greater than the speed of the flow of the gas, when even the first portions of the gas reduce the salt from the surface almost completely, and further portions will only dilute the gaseous mixture and thereby lessen the values obtained.• Therefore, in both cases, we will obtain values considerably lower than the true ones. Only in some rare cases, when the rate of flow of the gas, and the speed of the establishment of equilibrium are more or less commensurate, do the figures obtained by Jellinek agree with those of other authors; examples are the cases of $CoCl_2$ and $NiCl_2$ [21, 22].

DISCUSSION OF THE RESULTS

From the values obtained for the dissociation constants for the reaction of the reduction of CuHal with hydrogen and the equilibrium constants of the reaction of formation of the hydrogen halide, it is possible to obtain the values of the dissociation pressures of these compounds

$$2CuHal + H_2 = 2Cu + 2HHal,$$

$$K_e = \frac{P^2_{HHal}}{P_{H_2}} \text{ and } K_{HHal} = \frac{P^2_{HHal}}{P_{H_2} P_{Hal}},$$

$$P_{Hal_2} = \frac{P^2_{HHal}}{P_{H_2} K_{HHal}}, \quad P_{Hal_2} = \frac{K_e}{K_{HHal}}.$$

The values calculated in this way are given in Table 5.

From Table 5 it follows that

$$\log P_{Cl_2} = 5.012 - \frac{13809}{T} \text{ from } 250\text{-}350°C,$$

$$\log P_{Br_2} = 6.600 - \frac{11126}{T} \text{ from } 300\text{-}350°C.$$

The free energy, enthalpy, the entropy of formation of $CuCl_2$, CuCl, $CuBr_2$ and CuBr, calculated from the dissociation pressures, are given in Table 6. There is literature data for the thermal capacity of copper (I) and copper (II) chloride; therefore the values for ΔH and ΔS were given at 298°K for these compounds [23].

$$C_{P_{CuCl_2}} = 16 \cdot 80 + 0.0085 \cdot T,$$

$$C_{P_{CuCl}} = 10 \cdot 50 + 0.0097 \cdot T,$$

$$C_{P_{Cu}} = 5 \cdot 87 + 0.001 \cdot T - \frac{28700}{T^2},$$

$$C_{P_{Cl_2}} = 8 \cdot 77 + 0.00025 \cdot T.$$

On the formation of CuCl the entropy is lowered by 12.8 entropy units/mole, and on the formation of $CuCl_2$ by 32.9 entropy units/mole. The entropy of copper is equal to 7.97 entropy units/g-atom; the entropy of chlorine is equal to 53.31 entropy units/mole; hence the entropy of CuCl and $CuCl_2$ are equal, respectively, to 21.8 and 28.4 entropy units/mole.

In Fig. 5 is represented the dependence of the free energy of formation of the copper halides on the temperature. The free energy of formation of CuF_2, CuF and CuI were calculated from the data of Brewer's table [24]. The free energy of CuI_2 was calculated roughly by us from the formula ΔF = ΔH − TΔS, where ΔH is a value extrapolated by Britske and Kapustinsky [23] (ΔH = −4.8 kcal/mole; taking into account the heat of sublimation of iodine, we obtain a value for ΔH on the order of −20 kcal/mole). For the entropy of copper (II) iodide, by analogy with the compounds of the other metals of the same decade of the periodic system with iodine, we took a value of 39 entropy units/mole. The value of ΔF in the case of CuI_2 was, of course, very approximate, but the order of the curve nevertheless remained the same. In the case of the fluorides, the free energy of CuF_2 was considerably more

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• The work carried out by us to test Jellinek's method fully confirmed this hypothesis.

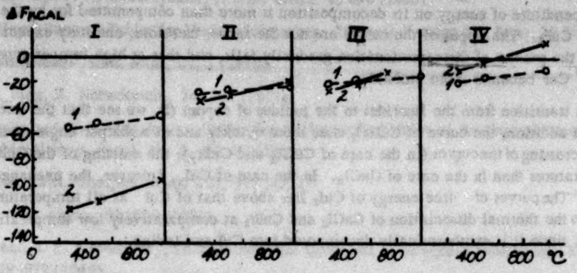

Fig. 5. Variation of the free energy of formation of copper halides with temperature. I) Fluorides: 1) CuF, 2) CuF_2; II) chlorides: 1) CuCl, 2) $CuCl_2$; III) bromides: 1) CuBr, 2) $CuBr_2$; IV) iodides: 1) CuI, 2) CuI_2.

TABLE 5

Temperature		CuCl			CuBr		
°C	°K	log K_e	log K_{HCl}	log P_{Cl_2}	log K_e	log K_{HBr}	log P_{Br_2}
250	523	−2.337	19.329	−21.666	−	−	−
300	573	−1.315	17.714	−19.029	−2.420	17.714	−12.816
315	588	−	−	−	−2.201	10.130	−12.331
325	598	−1.071	17.009	−18.080	−2.000	9.961	−11.961
340	613	−	−	−	−1.820	9.730	−11.550
350	623	−0.796	16.361	−17.157	−1.658	9.600	−11.258
375	648	−	−	−	−1.620	9.270	−10.890
400	673	−	−	−	−1.432	8.962	−10.392
401*	674	−0.286	15.185	−15.471	−	−	−
436	709	−0.061	14.482	−14.543	−	−	−
480	753	−	−	−	−1.222	8.113	− 9.335
507	780	+0.240	13.229	−12.989	−	−	−
550	823	−	−	−	−0.796	7.505	− 8.301
552	825	+0.340	12.546	−12.206	−	−	−
595	868	+0.535	11.963	−11.428	−	−	−
665	938	+0.736	11.131	−10.395	−	−	−
726	999	+0.878	10.487	− 9.609	−	−	−

TABLE 6

Substance	Temperature interval °K	ΔH kcal/mole	ΔS, entropy unit/mole**	$ΔF_{298}$ cal/mole	$ΔH_{298}$ kcal/mole	$ΔS_{298}$ entropy unit/mole
CuCl	523-623	−	−	−27732	−31.9	−12.8
$CuCl_2$	492-768	−	−	−31400	−41.2	−32.9
CuBr***	573-623	−25.4	−15.1	−21952	−	−
$CuBr_2$	403-589	−32.0	−26.3	−24210	−	−

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* Data for CuCl at 401° was taken from Watanabe [11].

** Entropy unit.

*** In the case of the bromides, all thermodynamic values were calculated for the formation of the bromide from gaseous bromine.

negative than the free energy of CuF; this leads us to the conclusion that CuF must undergo disproportionation, since the expenditure of energy on its decomposition is more than compensated for by the gain of energy on the formation of CuF_2. The slopes of the curves are not the same; therefore, one may expect that the exothermic character of the process of disproportionation gradually falls, and that at high temperatures the possibility of the existence of CuF becomes more probable.

With a transition from the fluorides to the iodides of copper (I), we see that the free energy curves rise higher and higher; in addition, the curve of $CuHal_2$ rises more quickly and at a sharper angle than the CuHal curve. This leads to the crossing of the curves (in the case of $CuCl_x$ and $CuBr_x$); the crossing of the $CuBr_x$ curves takes place at lower temperatures than in the case of $CuCl_x$. In the case of CuI_x, however, the exchange of places of the curves takes place. The curves of free energy of CuI_2 lies above that of CuI at all temperatures. Such a position of the curves leads to the thermal dissociation of $CuCl_2$ and $CuBr_2$ at comparatively low temperatures, and to the disappearance of CuI_2, since it is exothermically decomposed into CuI and iodine.

SUMMARY

1. The dissociation pressure of $CuCl_2$ was investigated by a statistical method in the temperature range from 219 to 495°C.

2. First, the dissociation pressure of $CuBr_2$ was investigated statistically in the temperature range from 130 to 316°C.

3. The equilibrium which was established on the reduction of CuCl with hydrogen in the temperature range from 250 to 350°C has been investigated.

4. The equilibrium which was established on the reduction of CuBr with hydrogen in the interval from 300 to 550°C has been investigated.

5. It has been shown that on the curve $\log K_e/1/T$ in the case of CuBr there are two inflections – one corresponding to the melting point of CuBr at 480°C, and the other at ~350°C, corresponding to the transition from one crystalline modification to another.

6. The enthalpy and the entropy of formation of $CuCl_2$, $CuBr_2$, CuCl and CuBr have been calculated.

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INVESTIGATION OF THE TERNARY SYSTEMS OF THE CHLORIDES, SULFATES AND TUNGSTATES OF LITHIUM AND POTASSIUM. I

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

The investigation of the ternary systems Li||Cl, SO_4, WO_4 and K||Cl, SO_4, WO_4 is one of a series of studies which we are carrying out on the tungstates of the alkali metals lithium and potassium. The purpose of these investigations is the clarification of the interrelationship between the double decomposition reaction and that of complex formation; this relationship determines the character of the diagrams of the systems. After studying these two factors in the ternary system Li, K||SO_4 WO_4, we established its character as a system of the adiagonal-zone type. [1] This system is one of the three outer faces of the quarternary system Li, K||Cl, SO_4, WO_4. The above-mentioned ternary systems Li||Cl, SO_4, WO_4 and K||Cl, SO_4, WO_4 are the upper and lower bases of a right triangular prism, in which form quarternary reciprocal systems are usually represented (Fig. 1) [2].

EXPERIMENTAL

The systems were investigated by the visual-polythermal method, which has a number of advantages in investigations of systems with three and four components [3]; this method has been sufficiently described in the literature [4]. We will give briefly the characteristics of the components of the investigated ternary systems, Li,|| Cl, SO_4, WO_4 and K||Cl, SO_4, WO_4:

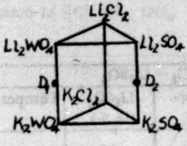

Fig. 1. Scheme of the prism Li, K||Cl, SO_4, WO_4.

Component	Melting point	Transformations
Lithium chloride	606°	Homeomorphic - 565°
Lithium sulfate	860	Heteromorphic - 572°
Lithium tungstate	738	Heteromorphic - 660°
Potassium chloride	774	Homeomorphic - 27, 374
Potassium sulfate	1069	–
Potassium tungstate	1926	–

The Ternary System of the Chlorides, Sulfates, and Tungstates of Lithium

The ternary system Li||Cl, SO_4, WO_4 enters into the composition of the quarternary system Li, K||Cl, SO_4, WO_4 and was studied as the upper triangular base of the right triangular prism. The binary lateral sides of the ternary system Li||Cl, SO_4, WO_4 consist of:

1) The system Li_2Cl_2-Li_2WO_4 studied by Bergman and Kislova, has a eutectic at 490° and 41.5% Li_2WO_4; the polymorphic transformation of Li_2WO_4 was noted at 660° and 77.5% Li_2WO_4 and the homeomorphic transformation of Li_2Cl_2 was noted at 565° and 16.5% Li_2Cl_2.

2) the system Li_2WO_4-Li_2SO_4 was studied by the same authors; the eutectic was established at 68% Li_2SO_4 and 596°; the side of Li_2WO_4 was complicated at 660° and 37.5% Li_2SO_4 by polymorphic transformation;

3) the system Li_2Cl_2-Li_2SO_4 studied by Klochko [5] and repeated by Bergman and Akopov [6].

The eutectic system consisted of two basic branches; on the branch of Li_2Cl_2 homeomorphic transformation takes place at 81.5% Li_2Cl_2 and 565°. The eutectic corresponds to 46.5% Li_2Cl_2 and 478°; on the branch of Li_2SO_4, polymorphic transformation takes place at 572° and 87.5% Li_2SO_4.

The characteristic points of these systems are given in Table 1.

The fusion diagrams of the binary systems are given in Fig. 2 and Table 2.

TABLE 1

Characteristic points of the binary systems

No.	Binary Systems	Characteristic points of the system	Our data		Data of other authors	
			(%)*	Melting point	(%)*	Melting point
1	$Li_2Cl_2 - Li_2WO_4$	Eutectic	41.5 Li_2WO_4	490°	–	–
		Polymorphic transformation	77.5 Li_2WO_4	660	–	–
		Polymorphic transformation	16.5 Li_2Cl_2	565	–	–
2	$Li_2WO_4 - Li_2SO_4$	Eutectic	68 Li_2SO_4	596	–	–
		Polymorphic transformation	37.5 Li_2SO_4	660	–	–
3	$Li_2Cl_2 - Li_2SO_4$	Eutectic	–	–	46.5 Li_2Cl_2	478° [5]
		Homeomorphic transformation	–	–	81.5 Li_2Cl_2	565
		Polymorphic transformation	–	–	87.5 Li_2SO_4	572

- In equilmolecular percentages of the added component.

TABLE 2

Binary systems

$Li_2Cl_2 - Li_2WO_4$		$Li_2WO_4 - Li_2SO_4$				$Li_2Cl_2 - Li_2SO_4$			
Li_2WO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature
0	606	0	738	57.5	620	0	606	88	610
5	592	2.5	734	60	614	6.3	593	90	628
10	580	5	730	62.5	608	11.9	582	93	695
15	568	7.5	724	65	600	18.0	566	95.5	740
20	552	10	720	68	596	24.5	555	100	852
25	540	12.5	716	70	614	31.1	538		
27	534	15	712	72.5	634	38.2	526		
30	524	17.5	705	75	652	40.4	520		
32	518	20	702	77.5	674	42.5	515		
35	512	22.5	696	80	690	44.5	509		
37	502	25	690	82.5	710	46.6	501		
40	496	27.5	685	85	734	48.7	495		
45	510	30	680	87.5	756	50.6	490		
50	530	32.5	674	90	776	52.5	482		
55	550	35	666	92.5	800	54.5	482		
60	580	37.5	660	95	818	56.1	488		
65	602	40	656	97.5	842	57.9	494		
70	626	42.5	652	100	860	60.6	503		
75	650	45	648			65.7	519		
77	660	47.5	644			70.7	538		
80	670	50	636			76.5	552		
85	692	52.5	634			82	568		
100	738	55	624			86	590		

Internal Cuts

The results of the investigation of 7 internal sections are given in Table 3 and on Fig. 3.

A Brief Description of the Cuts

Cut 1. 65% Li_2Cl_2 + 35% Li_2WO_4 → Li_2SO_4 intersects: β-Li_2Cl_2, β-Li_2WO_4, β-Li_2SO_4, α-Li_2SO_4, respectively at 450° and 20% Li_2SO_4, 450° and 43% Li_2SO_4, 572° and 82.5% Li_2SO_4.

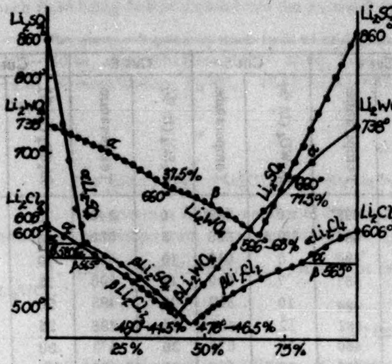

Fig. 2. The Binary Lateral Sides of the Ternary System Li ‖ Cl, SO_4, WO_4.

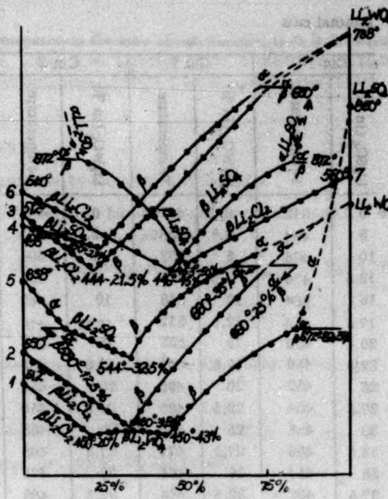

Fig. 3. Internal sections of the system Li ‖ Cl, SO_4, WO_4.

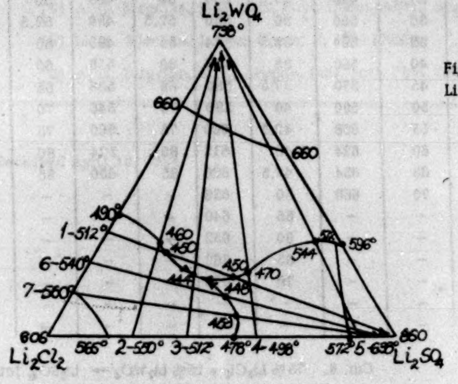
Li₂WO₄
738°
660
660
490
1-512°
6-540°
7-560°
460
460
450
470
444
448
468
544
576
596°
606
Li₂Cl₂
565°
2-580°
3-512°
478°
4-498°
572
5-638°
860
Li₂SO₄

Fig. 4. Direction of the internal cuts.

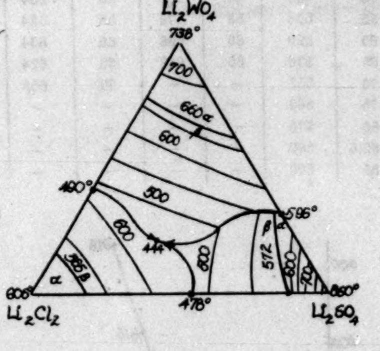
Li₂WO₄
738°
700
660α
β
600
490°
500
596°
600
444
600
572
β
600
700
565β
α
606°
Li₂Cl₂
478°
860°
Li₂SO₄

Fig. 5. Projection diagram of the system Li ‖ Cl, SO_4, WO_4 on the triangle of composition.

Cut 2. 75% Li_2Cl_2 + 25% $Li_2SO_4 \rightarrow Li_2WO_4$ intersects: β-Li_2Cl_2, β-Li_2WO_4, α-Li_2WO_4, respectively, at 460° and 31.5% Li_2WO_4, 660° and 75% Li_2WO_4.

Cut 3. 60% Li_2Cl_2 + 40% $Li_2SO_4 \rightarrow Li_2WO_4$ intersects: β-Li_2Cl_2, β-Li_2WO_4, α-Li_2WO_4, respectively, at 444° and 21.5% Li_2WO_4, 660° and 73% Li_2WO_4.

Cut 4. 40% Li_2Cl_2 + 60% $Li_2SO_4 \rightarrow Li_2WO_4$ passes through the field β-Li_2SO_4, β- and α-Li_2WO_4 at 470° and 23% Li_2WO_4, 660° and 70% Li_2WO_4.

Cut 5. 90% Li_2SO_4 + 10% $Li_2Cl_2 \rightarrow Li_2WO_4$ intersects: α-Li_2SO_4, β-Li_2SO_4, β-Li_2WO_4, α-Li_2WO_4 at 580° and 12.5% Li_2WO_4, 544° and 32.5% Li_2WO_4, 660° and 35% Li_2WO_4.

TABLE 3

Internal cuts

Cut 1		Cut 2		Cut 3		Cut 4		Cut 5		Cut 6		Cut 7	
Li_2SO_4 (in %)	Temperature	Li_2WO_4 (in %)	Temperature	Li_2WO_4 (in %)	Temperature	Li_2WO_4 (in %)	Temperature	Li_2WO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature
0	512°	0	550°	0	512°	0	498°	0	638°	0	540°	0	560°
5	494	2.5	538	2.5	503	2.5	494	2.5	628	5	530	5	550
10	478	5	532	5	594	5	490	5	616	10	518	10	540
12.5	470	7.5	525	7.5	485	7.5	487	7.5	600	15	506	15	530
15	464	10	518	10	480	10	484	10	592	20	495	20	518
17.5	458	12.5	512	12.5	475	12.5	482	12.5	580	25	486	25	505
20	450	15	505	15	465	15	480	15	576	30	475	30	494
22.5	450	17.5	500	17.5	458	17.5	477	17.5	572	35	466	35	482
25	452	20	495	20	450	20	474	20	568	40	456	40	470
27.5	454	22.5	485	22.5	450	22.5	472	22.5	562	45	448	45	462
30	456	25	480	25	458	25	478	25	557	47.5	456	47.5	457
32.5	456	27.5	474	27.5	468	27.5	490	27.5	554	50	468	50	453
35	454	30	464	30	475	30	500	30	550	52.5	480	52.5	462
37.5	452	32.5	464	32.5	485	35	524	32.5	544	55	490	55	480
40	452	35	478	35	498	40	550	35	566	60	518	60	510
42.5	450	37.5	490	37.5	508	45	570	37.5	580	65	536	65	530
45	458	40	508	40	518	50	590	40	590	70	546	70	550
47.5	470	45	530	45	540	55	608	42.5	600	75	560	75	564
50	484	50	550	50	564	60	624	45	612	80	574	80	580
55	504	55	578	55	584	65	634	47.5	620	85	600	85	600
60	520	60	698	60	604	70	660	50	628	–	–	–	–
65	536	65	618	65	624	–	–	55	640	–	–	–	–
70	552	–	–	70	650	–	–	60	652	–	–	–	–
75	562	–	–	–	–	–	–	65	662	–	–	–	–
80	575	–	–	–	–	–	–	70	672	–	–	–	–
82.5	580	–	–	–	–	–	–	–	–	–	–	–	–
85	600	–	–	–	–	–	–	–	–	–	–	–	–

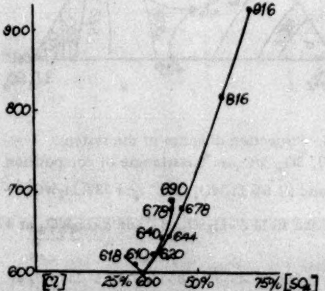

Fig. 6. Projection of the lines of common crystallization of the system Li ||Cl, SO_4, WO_4 on the side of $Li_2Cl_2 - Li_2SO_4$.

Cut. 6. 75% Li_2Cl_2 + 25% $Li_2WO_4 \rightarrow Li_2SO_4$, intersects: β-$Li_2Cl_2$, β- and α-$Li_2SO_4$ at 446° and 45% Li_2SO_4, 530° at 83% Li_2SO_4.

Cut 7. 85% Li_2Cl_2 + 15% $Li_2WO_4 \rightarrow Li_2SO_4$ passes through the fields β-Li_2Cl_2, β- and α-Li_2SO_4 at 453° and 50% Li_2SO_4, 572° at 85% Li_2SO_4.

Fig. 4 shows the scheme of the internal cuts.

Fig. 5 shows the projection diagram of the composition of the investigated ternary reciprocal system. Isotherms are given 50° apart; the polymorphic transformations of the components are shown correspondingly. In order to make the monovariant crystallization curves and the positions of the non-variant triple points in the system more exact, a projection of the common curves of crystallization of the triangle of composition on the $Li_2Cl_2 - Li_2SO_4$ side (Fig. 6), was constructed.

The diagram of the crystallization surface of the system consists of 3 fields of crystallization of the components, each field being further divided into the α- and β- sections.

The area, occupied by each field of crystallization, compared to the area of the triangle, is as follows (in %): LiCl – 26.44, α-modification, LiCl – 23.38, β-modification, LiCl – 3.06, Li_2WO_4 – 50.32, α-modification Li_2WO_4 – 8.81, β-modification, Li_2WO_4 – 41.51, Li_2SO_4 – 23.24, α-modification Li_2SO_4 – 4.94, β-modification Li_2SO_4 – 18.30.

SUMMARY

1. The ternary system Li‖Cl, SO_4, WO_4 has been investigated by the method of fusibility.

2. The system is simple, consists of 3 fields of crystallization with further division into the α- and β-modifications of the components. The largest area is occupied by the field Li_2WO_4 – 50.32%.

3. There is one triple eutectic point in the system at 444° of the composition 32% Li_2SO_4, 47% Li_2Cl_2, 21% Li_2WO_4.

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THE RECIPROCAL SYSTEM OF THE CHLORIDES AND SULFATES OF LITHIUM AND CALCIUM

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The considerable quantity of data which has been accumulated on chloride-sulfate exchange in melts makes apparent a certain periodicity, observed on the interaction of the chlorides and sulfates of various metals, depending on the position of the metals in the periodic system.

It is of particular interest to confirm experimentally the tendency, which has been noted previously, toward the weakening of complex-formation in reciprocal systems of the chloride-sulfate series of the mono- and divalent metals upon the systematic replacement of sodium and lithium by potassium in a system containing one and the same divalent metal [1-9].

The present investigation of the reciprocal system $Li,Ca \parallel Cl,SO_4$, along with the previously investigated systems $K,Ca \parallel Cl,SO_4$ [3] and $Na,Ca \parallel Cl,SO_4$ [4], makes this series complete.

At the same time, we have kept in mind the question of the confirmation of the correspondence between the conditionally calculated heat effect of the exchange reaction and the character of the diagram of the system [10].

EXPERIMENTAL•

The visual-polythermal method was utilized in the study of this system. The work was carried out in Pt crucibles in shaft electric furnaces. Thermocouples of alloys of Au,Pd,Pt-Pt,Rh were used. All compositions are expressed in equimolecular percentages. The melting points of the salts are: LiCl 609°, Li_2SO_4 852°, $CaCl_2$ 774°. The melting point of $CaSO_4$ has been taken conditionally from the literature [11] as being equal to 1450°.

Binary Systems

The previously studied systems: 1) Li_2Cl_2-Li_2SO_4 [12, 13], 2) Li_2Cl_2-$CaCl_2$ [14], 3) Li_2SO_4-$CaSO_4$ [15], 4) $CaCl_2$-$CaSO_4$ [16] were repeated by us. They are simple systems, with eutectics located, according to our data, at 480° and 52.5% Li_2SO_4 in the first of these systems, at 475° and 53% $CaCl_2$ in the second system, at 706° and 16.2% $CaSO_4$ in the third system, and at 708° and 12.5% $CaSO_4$ in the fourth system.

For the crystallization branches of $LiSO_4$ inflexions are observed in all cases at 572°; this corresponds to the heteromorphic transformation of this salt. On the branch of LiCl homeomorphic transformation occurs at 566°.

Diagonal sections. Studied previously [17] and repeated by us.
1. Li_2Cl_2-$CaSO_4$ is a stable diagonal section of the reciprocal system; the eutectic point, according to our data, is at 533° and 25% $CaSO_4$. 2. $CaCl_2$-Li_2SO_4 intersects the fields of the product of exchange of $CaSO_4$ respectively, according to our data, at 627° and 13.5% and 600° and 87.5% $LiSO_4$.

Internal cuts (Table 1 and Fig. 3). Eight internal cuts were studied; their distribution is shown on Fig. 2.

The crystallization surface of the reciprocal system (Fig. 4) is divided into the four crystallization fields of the components.

The largest single crystallization area (Table 2) occupies 76% of the total area; it is the field of the component with the highest melting point – $CaSO_4$.

Triangulation of the system into two-phase triangles is accomplished by means of the stable diagonal section Li_2Cl_2-$CaSO_4$.

With the projection of the curves of common crystallization on the sides of the composition area, a regular

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• With the participation of T. T. Logacheva.

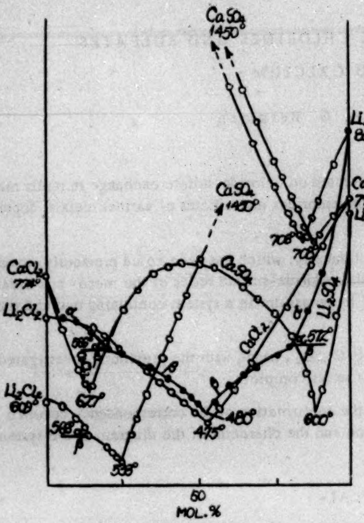

Fig. 1. Lateral sides and diagonal sections of the reciprocal system Li, Ca || Cl, SO$_4$.

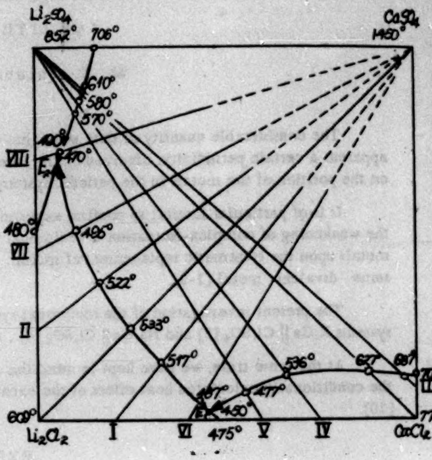
Li₂SO₄ 852°
706°
CaSO₄ 1450°
610°
580°
570°
VIII
470°
E₂
480°
495°
VII
522°
II
533°
517°
536°
627°
687°
708°
III
609°
487°
477°
450°
774°
Li₂Cl₂
I
VI
475°
V
IV
CaCl₂

Fig. 2. Distribution of the internal cuts in the system Li, Ca || Cl, SO$_4$.

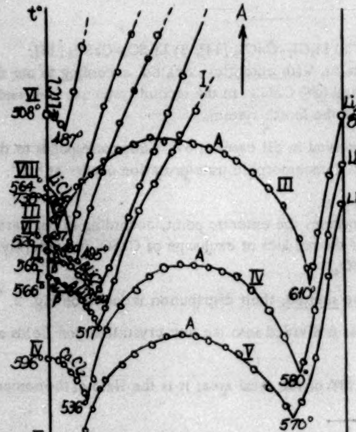

Fig. 3. Cuts through the reciprocal system Li, Ca|| Cl, SO$_4$.
Direction of cuts I, II, VI, VII and VIII toward CaSO$_4$. A) CaSO$_4$.

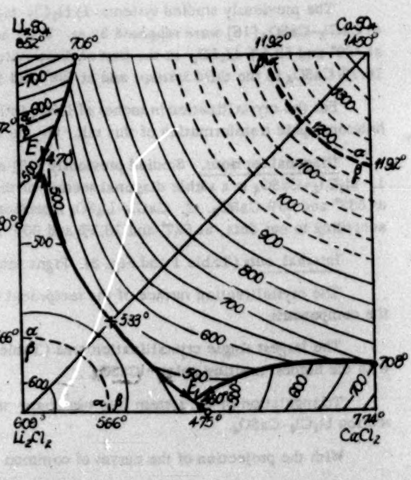
Li₂SO₄ 852°
706°
1192°
CaSO₄ 1450°
700
600
572°
E
470
1300
1200
1192°
1100
1000
900
800
700
600
480°
500
533°
566°
α
β
500
708°
600
480°
475°
609°
566°
774°
Li₂Cl₂
CaCl₂

Fig. 4. Projection of the three dimensional diagram of the reciprocal system Li, Ca || Cl, SO$_4$ on the composition square.

TABLE 1

A – Original composition, B – added component; in the first column is given the molecular percentage of the added component, in the second column, the temperature of the appearance of the first crystals

Cut I

A – 20% $CaCl_2$
80% Li_2Cl_2
B – $CaSO_4$

1	2
0	584
2.5	580
5	570
7.5	560
11	554
13	542
14	534
16	526
19.5	540
22	580
31	673
36	711
42	752
45	744
50	808
P• 17	517

Cut II

A – 25% $LiSO_4$
75% Li_2Cl_2
B – $CaSO_4$

1	2
0	584
2.5	577
5	568
7.5	562
10.5	550
12	546
13.5	541
15	528
18	531
22	562
28	628
32	672
36.5	720
41	768
46.5	820
54	900
P• 16.5	522

Cut III

A – 10% $CaSO_4$
90% $CaCl_2$
B – Li_2SO_4

1	2
0	738
2.5	706
5	716
7.5	736
10	750
15	766
20	785
25	800
30	812
35	817
40	816
45	815
50	813
55	806
60	800
65	790
70	772
75	750
80	726
85	684
87.5	646
90	650
95	770
P_1 3.5	687
P_2 88.5	610

Cut IV

A – 25% Li_2Cl_2
75% $CaCl_2$
B – Li_2SO_4

1	2
0	596
2.5	591
5	587
7.5	574
10	562
12.5	547
15	566
20	634
25	666
30	688
35	708
40	716
45	720
50	722
55	719
60	714
65	706
70	688
75	658
80	624
85	586
90	660
95	760
P_1 13	536
P_2 85	580

Cut V

A – 40% Li_2Cl_2
60% $CaCl_2$
B – Li_2SO_4

1	2
0	524
2.5	500
5	486
7.5	474
10	507
12.5	542
15	574
17.5	600
20	614
25	634
30	648
35	660
40	670
45	673
50	672
60	657
65	648
70	632
75	603
80	582
85	586
90	648
95	756
P_1 7.5	477
P_2 82.5	570

Cut VI

A – 40% $CaCl_2$
60% Li_2Cl_2
B – $CaSO_4$

1	2
0	508
2.5	503
5	494
10	540
12.5	600
P 6.2	487

Cut VII

A – 45% Li_2SO_4
55% Li_2Cl_2
B – $CaSO_4$

1	2
0	526
2.5	514
5	507
7.5	500
10	495
15	565
20	617
25	680
30	726
35	768
40	817
50	910
P 10	495

Cut VIII

A – 30% Li_2Cl_2
70% Li_2SO_4
B – $CaSO_4$

1	2
0	564
5	546
7.5	490
10	530
12.5	570
15	608
20	675
25	722
30	772
35	826
40	870
45	924
P 7.5	490

• P – Points of intersection of the crystallization curves.

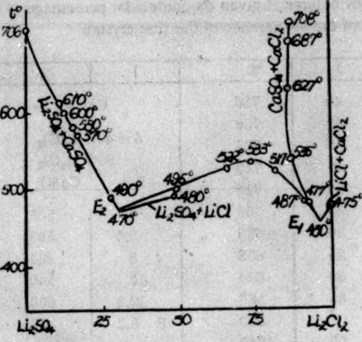

Fig. 5. Projection of the curves of common crystallization of the reciprocal system Li, Ca || Cl, SO_4 on the side of Li_2SO_4-Li_2Cl_2.

TABLE 2

Areas of the fields of crystallization

Name of the field of crystallization	Percentage of the total area occupied by the given field
$CaSO_4$	76
LiCl	14
Li_2SO_4	4.3
$CaCl_2$	5.7

fall in temperature and a full correspondence of the distribution of these curves and the multiple points is observed. One of these projections is shown in Fig. 5. The isotherms in the field of $CaSO_4$ form the clearly expressed ridge, deflecting somewhat in the direction of Li_2SO_4 from the plane of the stable diagonal; this shows a tendency toward an exchange reaction between the components of the stable pair.

The absence of complex-formation in this reciprocal system confirms, as was shown in the beginning of the present work, the tendency toward the weakening of complex-formation in reciprocal systems of the chloride-sulfate series of mono- and divalent metals in the systematic replacement of sodium and lithium by potassium.

According to the value for the conditional thermal effect of the reaction of exchange, calculated from the heat of formation of the salts as 1.58 kcal/gram-equivalent, this system should be reversible-reciprocal [10]; this, however, is not confirmed by its space diagram, which corresponds to the irreversible-reciprocal type.

Such a sharp lack of correspondence between the thermal effect of the reaction of exchange in a reciprocal system, and the character of its diagram indicates that: 1) either the conditional thermal effect of the exchange reaction, with small values for the thermal effect, is not always applicable for a priori judgment of the character of the reciprocal system, or 2) the available literature data on the heat of formation of some salts are not completely accurate.

SUMMARY

1. The reciprocal system Li, Ca || Cl, SO_4, which has been studied by the visual-polythermal method, is an irreversible-reciprocal system without complex-formation and has two triple eutectic points.

2. The absence of complex-formation in the system confirms the previously noted weakening of the tendency toward complex-formation in systems of the chloride-sulfate series of mono- divalent metals on the replacement of lithium and sodium by potassium, with one and the same divalent metal.

3. The lack of correspondence between the conditionally calculated thermal effect of the exchange reaction in the system and the character of its space diagram has been established.

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PHYSICO-CHEMICAL INVESTIGATION OF AQUEOUS DIOXANE SOLUTIONS

VI. DIOXANE SOLUTIONS OF HYDROGEN CHLORIDE

Ya. F. Mezhennyi

Kablukov [1], studying solutions of hydrogen chloride in solvents of different dielectric constants, established the existence of a dependence relationship between the electroconductivity and the dielectric constant of the medium (Kablukov's rule). Starting from Kablukov's rule it is possible to predict very small values for the electroconductivity of solutions of HCl in dioxane. The value for the electroconductivity should be less, for corresponding concentrations than that obtained by Kablukov for an ethereal solution of hydrogen chloride, and should approximate those obtained for benzene solutions of HCl.

1. Solubility of Hydrogen Chloride in Dioxane

The method of preparation and the properties of the dioxane utilized in these experiments have been described previously [2]. The hydrogen chloride was prepared by the interaction of sulfuric acid and chemically pure sodium chloride; it was dried with sulfuric acid.

The experiments showed that dry hydrogen chloride is very soluble in dioxane, completely colorless, transparent solutions being formed. As in the case of water, the process of solution of gaseous hydrogen chloride in dioxane is accompanied by the evolution of a considerable quantity of heat.

The determination of the solubility was carried out by the saturation of a weighed portion of dioxane (which had been placed in a thermostat) with hydrogen chloride until the weight was constant. It was established that the concentration of hydrogen chloride in a saturated solution at 20° was equal to 45.0 mole %, and the concentration of a saturated solution at 12° was 52.3 mole %.

In addition to the determination by the gravimetric method, the concentration of hydrogen chloride was also determined by the volumetric method, for which individual weighed portions of the solution were added to water in a calibrated flask up to 50 ml and titrated with a solution of sodium hydroxide in the presence of phenolphthalein. The quantity of hydrogen chloride in the dioxane solution, obtained by the volumetric method, coincided with the quantity of HCl found by gravimetric means.

2. Electroconductivity of Solutions of Hydrogen Chloride in Dioxane

The determination of the electroconductivity was carried out on an assembly with a metrically calibrated rheochord and telephone. The apparatus was supplied with power by a tube generator of audible frequency. An air condenser of variable capacity was connected in parallel with the resistance box. The vessel for the measurement of the electroconductivity consisted of a small cylinder with rigidly soldered platinum-plated platinum electrodes. In order to prevent the evaporation of the solutions and the falling of moisture into them, the vessel was closed with a ground-glass stopper with an elongated polished section. The length of the polished section was 2.5 cm. Besides being sealed with a ground-in cover, the vessel was closed with a dry rubber cap. The calibration of the vessel was carried out by means of an aqueous potassium chloride solution. The data obtained on the electroconductivity of dioxane solutions of hydrogen chloride are given below.

TABLE 1

Electroconductivity of solutions of hydrogen chloride in dioxane at 20°

c (gram-equivalent/liter)	v (liter/gram-equivalent)	κ	$\lambda \cdot 10^{-3}$
0	–	$< 10^{-8}$	–
3.343	0.290	$< 10^{-8}$	–
5.610	0.178	$< 10^{-8}$	–
7.670	0.133	$2.52 \cdot 10^{-6}$	0.336
7.740	0.129	$5.26 \cdot 10^{-6}$	0.673

As is evident from the data given in Table 1, hydrogen chloride, while a strong electrolyte in aqueous solutions, is by no means a strong electrolyte on its dissolution in dioxane, its dielectric constant in the latter case being 36 times less than in the case of its dissolution in water. From the data of Table 1 it is evident that in dioxane solutions with a concentration of 3.34 N, and even of 5.61 N, the electroconductivity of this system differs by only a small amount from the electroconductivity of pure distilled water. Only beginning with 7.67 N (which corresponds to 43.2 mole % HCl) does the specific electroconductivity reach a magnitude of the order of a millionth part, and the equivalent electroconductivity reach a magnitude of the order of a ten-thousandth part, of the order of the electroconductivity of distilled water. At the same time, for aqueous solutions of HCl, at these concentrations the specific electroconductivity reaches values of the order of 0.7 and the equivalent electroconductivity reaches values of about 150 reciprocal ohms. Therefore, in regard to electroconductivity, solutions of hydrogen chloride in dioxane are thousands of times weaker than even such weak electrolytes in water as acetic acid; the equivalent electroconductivity of the latter, at a concentration of 5 g-mole/liter in water, is 0.28; HCl in dioxane has an electroconductivity of only $0.3 \cdot 10^{-8}$ reciprocal ohms.

One more fact attracts our attention. As is evident from the data of Table 1, the equivalent electroconductivity of hydrogen chloride in dioxane increases with the concentration, and therefore, falls upon dilution. In other words, we have here a typical "anomalous curve" $\lambda = f(v)$.

3. Cryoscopy of Dioxane Solutions of Hydrogen Chloride

It is evident from the data of the investigation of the electroconductivity of solutions of hydrogen chloride in dioxane, that this solution dissociates only very slightly, and that hydrogen chloride in dioxane, unlike the case of its solutions in water, is a very, very weak electrolyte, or even a non-electrolyte.

In connection with the practically negligible dissociation of the hydrogen chloride molecules it was interesting to establish its molecular weight in dioxane; for this purpose, cryoscopic methods were used, giving, as is known, for aqueous solutions of HCl $\Delta t_{experimental} > \Delta t_{theoretical}$; $M_{experimental} < M_{theoretical}$. Starting from the data on the electroconductivity of HCl, in dioxane, one might expect in this case that $M_{experimental} > M_{theoretical}$.

The systems for the cryoscopic measurements were prepared in the following way. First, the temperature of crystallization of pure dioxane was determined in the cryoscopic apparatus; then a definite quantity of a previously prepared dioxane solution of hydrogen chloride, with a known HCl content, was introduced. Further changes in the ratio of the components of the solution were brought about by the addition of definite quantities of dioxane, as is evident from the first column of Table 2.

TABLE 2

Determination of the molecular weight of hydrogen chloride in dioxane by the cryoscopic method

Expt. No.	Weight of dioxane G (in g)	Dissolved HCl g (in g)	Lowering of the temperature of crystallization $\Delta t_{expt.}$	$M_{expt.} = 4.83 \cdot \frac{1000 \cdot g}{\Delta t_{expt.} \cdot G}$	$x = \frac{M_{expt.}}{M_{theo.}}$
1	6.420	0	0.00	–	–
2	6.431	0.3489	6.32	41.5	1.15
3	7.383	0.3489	5.50	41.7	1.13
4	8.344	0.3489	4.91	40.8	1.11
5	10.693	0.3489	3.69	42.6	1.158
6	12.651	0.3489	3.11	42.9	1.163
7	13.481	0.3489	2.82	46.3	1.25
8	15.224	0.3489	2.44	46.1	1.25
9	16.235	0.3489	2.17	49.4	1.34
10	17.359	0.3489	2.20	54.06	1.46
11	19.286	0.3489	2.25	39.2	1.07
12	21.218	0.3489	1.76	45.1	1.23
13	5.31	0.3489	0.00	–	–
14	5.779	0.0731	1.43	42.5	1.16
15	6.749	0.0731	1.22	42.8	1.17
16	7.090	0.0731	0.99	50.3	1.37
17	7.531	0.0731	0.92	50.3	1.37

It is evident from the data of Table 2 that in all the investigated cases in the interval of the depression of the freezing point up to 6.32° (which corresponds to concentrations of up to 1000 mole of hydrogen chloride per 1.5 g of dioxane), the molecular weight of HCl proved to be higher than the theoretical value.

This can be explained either by the partial association of the hydrogen chloride molecules according to the equation

$$xHCl \rightleftharpoons (HCl)x, \tag{1}$$

or by the formation of complex ions through the combing of ions with undissociated molecules:

$$HCl \rightleftharpoons H^{\cdot} + Cl^{\prime} \tag{2}$$

$$H^{\cdot} + HCl \rightleftharpoons H_2^{\cdot}Cl \tag{3}$$

$$Cl^{\prime} + HCl \rightleftharpoons HCl_2^{\prime} \tag{4}$$

or, summarizing,

$$3HCl \rightleftharpoons H_2^{\cdot}Cl + HCl_2^{\prime}. \tag{5}$$

If, however, we assume the association of neutral molecules, even if only three of them, equations (1, 2, 3) may be represented by the equation:

$$(HCl)_3 \rightleftharpoons H_2^{\cdot}Cl + HCl_2^{\prime}. \tag{6}$$

If the equilibrium took place according to equation (2), corresponding to an aqueous solution of hydrogen chloride, then we would have the case $M_{experimental} < M_{theoret.}$ and $\Delta t_{experimental} > \Delta t_{theoretical}$. In view of the fact that the molecular weight, according to cryoscopic data, turns out to be greater than the theoretical, there is no basis for assuming the scheme of simple dissociation (equation 2) and the presence, in a dioxane solution of hydrogen chloride, of the simple ions $H^{\cdot}$ and $Cl^{\prime}$.

Nor is there any basis for considering that the state of the dissolved molecules of hydrogen chloride is described only by the equilibrium represented by equation (1), even if it is shifted strongly to the left (monomeric molecules), since this would disagree with the data on the electroconductivity of this system. Although the value for the electroconductivity is insignificant in absolute terms, its relative magnitude is, nevertheless, observed; therefore, it is most probable that the equilibrium in this system conforms to equations (1, 5, 6).

TABLE 3

Thermal analysis of the system hydrogen chloride – dioxane

HCl (in mole %)	Crystallization temperature
0	11.7°
3.78	9.9
4.14	9.5
4.55	9.5
4.75	9.53
5.2	9.0
5.8	8.2
7.2	7.6
9.0	6.4
10.1	5.8
11.5	5.0

4. Thermal Analysis of the System Hydrogen Chloride – Dioxane

We investigated only that branch of the curve embracing the comparatively small interval of hydrogen chloride concentration represented in Table 3.

From the data of Table 3 it is evident that the addition of increasing quantities of hydrogen chloride to the dioxane depresses the crystallization temperature of the solution more and more, the depression of the freezing point of a solution of HCl in dioxane in the investigated region (up to 11 mole % HCl), having almost a linear character.

5. Comparison of the Conductivity of Solutions of Hydrogen Chloride in Dioxane and in other Solvents

Uniting our data with the results of Kablukov's investigations, we obtain the picture presented in Table 4.

TABLE 4

Electroconductivity of solutions of hydrogen chloride in various solvents

Solvent	Dielectric constant ϵ	Dilution (l/mole)	λ	Investigator
Dioxane	2	0.29	A trace	The author
		0.178	the same	
		0.133	0.0003	
		0.129	0.000673	
Benzene	2.29	–	A trace	I. A. Kablukov [3]
Ethyl ether	4.37	3.52	0.00004	
Ethyl alcohol	25.4	100	27.17	
Methyl alcohol	35.4	91.16	117.06	
Water	81	100	394	

As we see from the data of Table 4, our data, in full agreement with that of Kablukov, again confirms the great importance of the ϵ of the medium, both as a factor changing the strength of an electrolyte, and as a factor converting a strong electrolyte in an aqueous medium into a weak electrolyte in alcohol, a very weak electrolyte in ether, and almost into a non-electrolyte in dioxane and benzene.

SUMMARY

1. Hydrogen chloride is very soluble in dioxane, since at 20° its content in the system can reach 45 mole %, and at 12° it can even reach 52 mole %. The dissolution of hydrogen chloride in dioxane is an exothermic process and is accompanied by the evolution of a considerable quantity of heat.

2. The equivalent electroconductivity of dilute solutions of HCl in dioxane $< 10^{-7}$ reciprocal ohms; only with $c \approx 7$ gram-equivalents/liter does it reach values of the order of 10^{-4} which is a million times less than the electroconductivity of HCl in aqueous solutions. The equivalent electroconductivity of hydrogen chloride in dioxane falls with dilution.

3. It has been shown by cryoscopic means that unlike aqueous solutions of HCl, the observed molecular weight of hydrogen chloride in dioxane is greater than the theoretical value. In accordance with the data on electroconductivity, this causes us to recognize the presence of polymerization (association) of hydrogen chloride molecules in dioxane solutions.

4. The composition – melting point curve of the system dioxane – hydrogen chloride, has been investigated from pure dioxane, up to the system containing about 12 mole % HCl. The almost linear character of this curve for the investigated region has been shown.

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THE MOLECULAR HEAT CAPACITY OF ORGANIC COMPOUNDS OF VARIOUS DEGREES OF HYDROGENATION

V. I. Kuznetsov

In one of my previous papers [1], I have shown that among the values for the molecular heat capacity of liquid hydrocarbons of various degrees of hydrogenation there exists a certain periodicity. Attention was attracted to the fact that the decrease in molecular heat capacity after the dehydrogenation of saturated hydrocarbons to mono-unsaturated hydrocarbons is a more or less constant value. Further dehydrogenation, however, evidently leads to a more rigid molecular structure, and, as a consequence of this, the heat capacity of the substance is lowered more sharply. This alone indicates new possibilities for the evaluation of the character of the structure of hydrocarbon molecules by means of the measurement of the heat capacity of these molecules. For ethane it turned out to be possible [2] to use another method, namely, the comparison of the calculated and measured heat capacity, which unconditionally revealed the entire picture of the structure and energy state of the molecule. This method is not applicable to more complicated molecules, since it would be impossible to take into account all the frequencies of natural oscillation in this case, and therefore the use of quantum formulas for the calculation of the heat capacity would also be impossible. Therefore, the utilization of the heat capacity as one of the criteria for the evaluation of the structure and energetics of complex molecules cannot be applied in all cases; it turns out that the most useful method for their utilization is the measurement of the heat capacity of substances whose structures are comparable.

From this point of view, in the present communication we have examined new cases of changes in the molecular heat capacity of organic compounds of various degrees of hydrogenation, and we have made more precise the various hypotheses expressed in the preceding paper. On the investigation of the heat capacity of the heavier liquid hydrocarbons, beginning with C_{10} and higher, it turned out that ΔC_M reaches values above 30, which essentially completes the table.

	Hydrocarbons					
	$C_{12}H_{26}$	$C_{12}H_{24}$	$C_{13}H_{28}$	$C_{13}H_{26}$	$C_{14}H_{30}$	$C_{14}H_{28}$
Magnitudes of the molecular heat capacity	355	321	385	347	402	372
ΔC_M	34		38		30	

Thus, the dehydrogenation of hydrocarbons, with the elimination of only two hydrogen atoms, lessens the molecular heat capacity to a greater extent than the transition to the next lower homolog. For example:

$$\begin{tikzcd}
 & C_{11}H_{24} \\
C_{12}H_{26} \arrow[ur, "-(CH_2)"] \arrow[dr, "-2H"'] & C_M = 327.00 \\
C_M = 355.30 & C_{12}H_{24} \\
 & C_M = 320.88
\end{tikzcd}$$

ΔC_M varies, however, within wide limits, for the value of the molecular heat capacity of various organic compounds. For oxygen-containing compounds, it is, as a rule, lower for high-molecular compounds, and, on the other hand, higher for low-molecular compounds:

$$\underset{C_M = 273.62}{C_4H_9-COOCH_2-CH_2-CH_3} \xrightarrow{-2H} \underset{C_M = 267.95 \quad \Delta C_M = 5.67}{C_4H_9COOCH_2-CH=CH_2}$$

$$C_3H_7-COOC_3H_7 \xrightarrow{-2H} C_3H_7-COOC_3H_5$$
$$C_M = 249.73 \qquad C_M = 241.53 \quad \Delta C_M = 8.20$$

$$CH_3COOC_3H_7 \xrightarrow{-2H} CH_3COOC_3H_5$$
$$C_M = 195.94 \qquad C_M = 180.20 \quad \Delta C_M = 15.74$$

$$C_3H_7OOC-COOC_3H_7 \xrightarrow{-4H} C_3H_5OOC-COOC_3H_5$$
$$C_M = 315.29 \qquad C_M = 303.11 \quad \Delta C_M = 12.18$$

The heat capacity of the esters of benzoic acid occupies a special place:

$$C_6H_5COOC_3H_7 \xrightarrow{-2H} C_6H_5COOC_3H_5$$
$$C_M = 273.22 \qquad C_M = 263.09 \quad \Delta C_M = 10.13$$

The examples which have been given indicate that the double bond which appears as a result of dehydrogenation leaves its imprint on the whole molecule, lowering both the number of oscillators and the amplitude of natural oscillations, i. e., it gives to the molecule rigidity of structure. If the molecule by itself has a sufficiently rigid structure, and it is therefore impossible to lower sharply the number of oscillators in it by the introduction of a double bond, the fall in its heat capacity on dehydrogenation is insignificant:

$$C_6H_5-CH_2-CH_2-CH_3 \xrightarrow{-2H} C_6H_5-CH-CH=CH_2$$
$$C_M = 200.88 \qquad C_M = 193.99 \quad \Delta C_M = 6.89$$

Especially interesting is the comparison of the heat capacity of those substances whose chemical structure is basically changed upon dehydrogenation. We will examine three cases of dehydrogenation of this type.

1. Dehydrogenation of Ethane

$$H_3C-CH_3 \xrightarrow{-2H} H_2C=CH_2 \xrightarrow{-2H} HC\equiv CH$$
$$C_M = 48.55 \qquad C_M = 42.14 \qquad C_M = 41.72$$
$$\Delta C_M = 6.41 \qquad \Delta C_M = 0.42$$

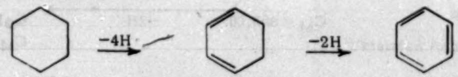
The step by step dehydrogenation of ethane to ethylene and then to acetylene leads to the above picture.

2. Dehydrogenation of n-Hexane

$$C_2H_5-CH_2-CH_2-CH_2-CH_3 \rightarrow C_2H_5-CH_2-CH_2-CH=CH_2 \rightarrow C_2H_5-CH=CH-CH=CH_2$$
$$C_M = 189.63 \qquad C_M = 177.81 \qquad C_M = 150.00$$
$$\Delta C_M = 11.82 \qquad \Delta C_M = 27.81$$

Here the fall in the molecular heat capacity takes place over both steps of dehydrogenation, the fall being sharper in the second step.

3. Dehydrogenation of Cyclohexane



$$C_M = 176.00 \qquad C_M = 100.41 \qquad C_M = 134.00$$
$$\Delta C_M = 75.59 \qquad +\Delta C_M = 33.59$$

In this case the dehydrogenation in the first step leads to a sharp lowering of the molecular heat capacity.* In the second step, on the other hand, dehydrogenation leads to an increase in the molecular heat capacity.

All three cases, showing one and the same process of dehydrogenation, indicate, however, three different directions of the change of molecular heat capacity. The exceptional disproportion of these changes indicates very clearly that the loss of molecular heat capacity takes place here least of all on account of the loss of hydrogen, and, therefore, of the decrease in the number of CH-oscillators in the molecule. The chief cause of the change is undoubtedly connected with the structure and energy state of the molecule.

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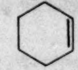
* Dehydrogenation of n-hexane to hexadiene lowers the molecular heat capacity only by 39.63 Joules/moles degrees, while here it is lowered by 75.59.

The great difference between the heat capacity of ethane and ethylene is explained by the loss of torsion vibration (or free rotation) of the methyl groups on the dehydrogenation of ethane, as was shown by Teller and Weigert [2]. Further dehydrogenation did not show any essential influence on the character of the natural oscillations of the molecule, and therefore the insignificant difference between the molecular heat capacities of ethylene and acetylene is explained no more as the loss of two CH-oscillators.

The progressive loss of molecular heat capacity on the dehydrogenation of n-hexane occurs as a consequence of the fact that the formation of each new double bond makes the structure of the molecule less and less mobile. It is also fully evident that at 20° in normal hexane, hexene, and hexadiene, the free rotation of radical groups around the axis of the C–C bond is absent. The most convincing proof of this is the comparison of the molecular heat capacity of hexene, cyclohexane, representing a closed system, and hexadiene.

$C_4H_9-CH=CH_2$

$C_M = 177.81$



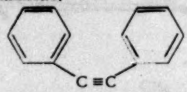
$C_M = 176.00$

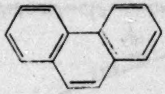
$C_2H_5-CH=CH-CH=CH_2$

$C_M = 150.00$

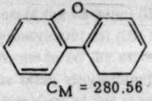
But most interesting is the raising of the molecular heat capacity on the dehydrogenation of cyclohexadiene to benzene. In spite of the loss of two hydrogen atoms, and, therefore, the apparent lowering of the number of oscillators, the molecular heat capacity of benzene turns out to be greater than that of cyclohexadiene; this indicates that the aromatic ring has a less rigid and taut structure than the unsaturated cyclic compounds.

The measured molecular heat capacity can also be used for the determination of whether, in a given molecule, torsion oscillation or free rotation along the C–C axis takes place, as in the case of ethane. For this purpose it is necessary to compare the molecular heat capacities of open and closed systems having the same number of oscillators, for example, tolane and phenanthrene:

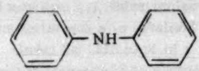




each of which contains 4 non-hydrogenated atoms and 10 CH-groups. There is, as yet, no data on the heat capacity of these particular substances. However, the heat capacity has been measured (at 30 and 50°, respectively, for the liquid state) of diphenyl oxide and diphenylamine.



$C_M = 280.56$



$C_M = 292.44$ $\Delta C_M = 11.88$

The comparison of the data on these two compounds confirms the existence of torsion oscillation of the nuclei in diphenylamine, and the relative rigidity of the closed system of diphenyl oxide.

SUMMARY

Additional data has been presented indicating the possibility of the use of the measured heat capacity of organic compounds for the evaluation of the structure and natural oscillations of molecules.

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DERIVATIVES OF ACETYLENE

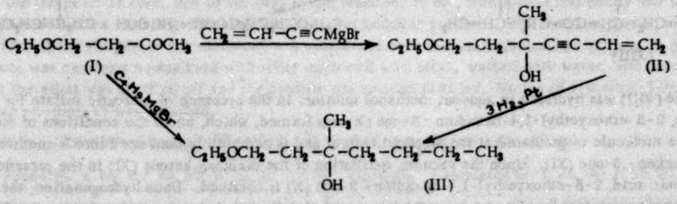
161. SYNTHESIS AND TRANSFORMATIONS OF METHYL-β-ETHOXYETHYLVINYLETHINYLCARBINOL

I. N. Nazarov, S. A. Vartanyan, and V. N. Zhamagortsyan

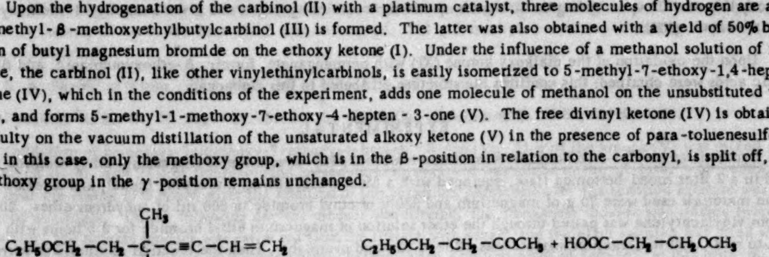
In our preceding work we described the synthesis and transformations of vinylethinylcarbinols containing methoxy groups [1]. It was of interest to explain the possibility of the synthesis of methyl-β-ethoxyethylvinylethinylcarbinol and to study its transformations for the purpose of clarifying the influence of the ethoxy group on the chemical activity of this carbinol.

Unlike aliphatic [2], alicyclic [3], and heterocyclic [4] ketones, methyl-β-ethoxyethyl ketone (I) proved to be completely incapable of entering into a condensation reaction with vinylacetylene in the presence of powdered potassium hydroxide; along with this, similar to other β-alkoxy ketones [5], it thickened completely into a sticky, non-distillable mass.

The synthesis of the carbinol (II) was carried out by us through the use of an organometallic compound. Upon the action of magnesium bromovinylacetylene on methyl-β-ethoxyethyl ketone (I), which was obtained by the hydration of vinyl acetylene in ethyl alcohol, methyl-β-ethoxyethylvinylethinylcarbinol(II) was obtained in a yield of about 90%.

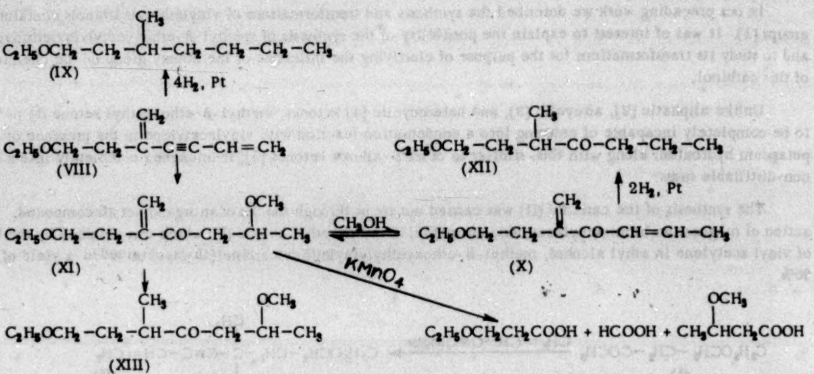

$C_2H_5OCH_2-CH_2-COCH_3$
(I)
$CH_2=CH-C\equiv CMgBr$
$C_2H_5OCH_2-CH_2-C(CH_3)(OH)-C\equiv C-CH=CH_2$
(II)
C_4H_9MgBr
$3H_2$, Pt
$C_2H_5OCH_2-CH_2-C(CH_3)(OH)-CH_2-CH_2-CH_2-CH_3$
(III)

Upon the hydrogenation of the carbinol (II) with a platinum catalyst, three molecules of hydrogen are absorbed and methyl-β-methoxyethylbutylcarbinol (III) is formed. The latter was also obtained with a yield of 50% by the action of butyl magnesium bromide on the ethoxy ketone (I). Under the influence of a methanol solution of mercuric sulfate, the carbinol (II), like other vinylethinylcarbinols, is easily isomerized to 5-methyl-7-ethoxy-1,4-heptadien-3-one (IV), which in the conditions of the experiment, adds one molecule of methanol on the unsubstituted vinyl group, and forms 5-methyl-1-methoxy-7-ethoxy-4-hepten-3-one (V). The free divinyl ketone (IV) is obtained with difficulty on the vacuum distillation of the unsaturated alkoxy ketone (V) in the presence of para-toluenesulfonic acid; in this case, only the methoxy group, which is in the β-position in relation to the carbonyl, is split off, while the ethoxy group in the γ-position remains unchanged.


$C_2H_5OCH_2-CH_2-C(CH_3)(OH)-C\equiv C-CH=CH_2$
(II)
$HgSO_4$
$C_2H_5OCH_2-CH_2-C(CH_3)=CH-CO-CH=CH_2$
(IV)
CH_3OH
$C_2H_5OCH_2-C-H_2C(CH_3)=CH-CO-CH_2-CH_2OCH_3$
(V)
$2H_2$, Pt
H_2, Pt
$KMnO_4$
$C_2H_5OCH_2-CH_2-COCH_3 + HOOC-CH_2-CH_2OCH_3$
$C_2H_5OCH_2-CH_2-CH(CH_3)-CH_2-CO-CH_2-CH_3$
(VI)
$C_2H_5OCH_2-CH_2-CH(CH_3)-CH_2-CO-CH_2CH_2OCH_3$
(VII)

Upon hydrogenation with a platinum catalyst, the divinyl ketone (IV) takes up two molecules of hydrogen and is transformed into 5-methyl-7-ethoxyheptan-3-one (VI); the analogous hydrogenation of the unsaturated methoxy ketone (V) leads to the taking up of one molecule of hydrogen and gives 5-methyl-1-methoxy-7-ethoxyheptan-3-one (VII). The structure of the methoxy ketone (V) was definitely established through the use of oxidation; upon oxidation, methyl-β-ethoxyethyl ketone (I) and β-methoxypropionic acid were obtained.

β-Ethoxyvinylethinylcarbinol (II) dehydrates easily on treatment with 50% sulfuric acid at 60° for 1.5 hours; it gives a mixture of dienes which is mainly 2-β-ethoxyethyl-1,5-hexadien-3-yne (VIII). Apparently the β-ethoxyethyl radical is involved in the dehydration of the carbinol (II) to only an insignificant degree. Upon hydrogenation in an alcoholic solution in the presence of a platinum catalyst, the dienyne (VIII) takes up four molecules of hydrogen and is converted into 3-methyl-1-ethoxyheptane (IX).


CH₃
C₂H₅OCH₂–CH₂–CH–CH₂–CH₂–CH₂–CH₃
(IX)
4H₂, Pt
CH₂
C₂H₅OCH₂–CH₂–C–C≡C–CH=CH₂
(VIII)
CH₃
C₂H₅OCH₂–CH₂–CH–CO–CH₂–CH₂–CH₃
(XII)
2H₂, Pt
CH₂
OCH₃
C₂H₅OCH₂–CH₂–C–CO–CH₂–CH–CH₃
(XI)
CH₃OH
CH₂
C₂H₅OCH₂–CH₂–C–CO–CH=CH–CH₃
(X)
KMnO₄
CH₃
OCH₃
C₂H₅OCH₂–CH₂–CH–CO–CH₂–CH–CH₃
(XIII)
OCH₃
C₂H₅OCH₂CH₂COOH + HCOOH + CH₃CHCH₂COOH

The dienyne (VIII) was hydrated in aqueous methanol solution in the presence of mercuric sulfate for 25 hours at 63°; thereupon, 2-β-ethoxyethyl-1,4-hexadien-3-one (X) was formed, which, under the conditions of the experiment adds one molecule of methanol at the propenyl radical and is completely converted into 5-methoxy-2-β-ethoxyethyl-1-hexen-3-one (XI). Upon the vacuum distillation of the dialkoxy ketone (XI) in the presence of para-toluenesulfonic acid, 2-β-ethoxyethyl-1,4-hexadien-3-one (X) is obtained. Upon hydrogenation, the ethoxydienone (X) takes up two molecules of hydrogen and is converted into 3-methyl-1-ethoxyheptan-4-one (XII); the dialkoxy ketone (XI) upon hydrogenation takes up one molecule of hydrogen and gives 5-methyl-2-methoxy-7-ethoxyheptan-4-one (XIII).

Upon the oxidation of the dialkoxy ketone (XI) with permanganate, formic, β-ethoxypropionic, and β-methoxybutyric acids were obtained; this confirms the structure attributed to this compound.

EXPERIMENTAL

Synthesis of methyl-β-ethoxyethylvinylethinylcarbinol (II). A solution of magnesium ethyl bromide was prepared in a 2 liter round-bottomed flask, equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser; the materials used were 70 g of magnesium and 330 g of ethyl bromide in 600 ml of anhydrous ether. 200 g of gaseous vinylacetylene was passed through the ether solution of magnesium ethyl bromide for 2.5 hours with cooling down to −18°, and the reaction mixture was allowed to stand overnight. Then the reaction mixture was stirred for one hour at room temperature and for 40 minutes at the boiling point of the ether, until the evolution of ethane had ceased completely. 230 g of methyl-β-ethoxyethyl ketone was added by drops over the course of 6 hours to the magnesium bromovinylacetylene which was obtained. During the time of the addition of the ketone, the temperature of the reaction mixture varied between −18 and +5°. The following day the reaction mixture was stirred for one hour at room temperature and for 40 minutes at the boiling point of the ether. The reaction product was hydrolyzed with 10% hydrochloric acid (1060 ml) while being cooled with ice water. The ether layer was separated, the product was neutralized with a 5% soda solution, washed with water, and dried with sodium sulfate. After the distillation of the ether, 300 g of methyl-β-ethoxyethylvinylethinylcarbinol was obtained.

B. p. 88-90° at 4 mm, d_4^{20} 0.9260, n_D^{20} 1.4740, MR_D 51.00; calc. 49.08.

Found %: C 71.37, 71.10; H 9.95, 9.77. $C_{10}H_{16}O_2$. Calculated %: C 71.42; H 9.52.

The obtained carbinol was a colorless, mobile liquid with a characteristic odor; upon being allowed to stand without a stabilizer, it thickens and is converted into a yellow glass-like polymer.

Hydrogenation of methyl-β-ethoxyethylvinylethinylcarbinol. 3 g of the freshly-distilled carbinol (II) in 10 ml of ethyl alcohol was hydrogenated in the presence of a platinum catalyst. The volume of hydrogen taken up was 1.3 l (calculated 1.21 l). 2.3 g of methyl-β-ethoxyethylbutylcarbinol (III) was obtained in the form of a colorless liquid with a pleasant odor.

B. p. 83° at 5 mm, d_4^{20} 0.8690, n_D^{20} 1.4350, MR_D 52.23; calc. 51.55.

Found %: C 69.02, 68.85; H 12.85, 12.88. $C_{10}H_{22}O_2$. Calculated %: C 68.95; H 12.64.

The action of butyl magnesium bromide on methyl-β-ethoxyethyl ketone (I). The butyl magnesium bromide was prepared in the usual manner from 15 g of butyl bromide and 2.6 g of magnesium in 60 ml of anhydrous ether. Then, 12 g of methyl-β-ethoxyethyl ketone was added by drops, over the course of an hour, with cooling to 0° and constant stirring. The stirring was continued for another hour at room temperature and for 30 minutes at the boiling point of the ether. The reaction product was hydrolyzed with 10% hydrochloric acid (40 ml) upon cooling with water. The ether layer was separated, neutralized with a 5% soda solution, washed with water and dried with sodium sulfate. After the driving off of the ether, the residue was vacuum distilled; 9.3 g of the above-described methyl-β-ethoxyethylbutylcarbinol (III) was obtained.

B. p. 93-94° at 10 mm, d_4^{20} 0.8755, n_D^{20} 1.4360.

Isomerization of methyl-β-ethoxyethylvinylethinylcarbinol (II). A mixture of 41 g of the freshly-distilled carbinol (II) which had been stabilized with pyrogallol, 120 g of distilled methanol, and 2 g of finely-ground mercuric sulfate were mixed and heated for 8 hours. In the beginning of the reaction, the temperature was raised to 55°, then the temperature rose, due to the heat of the reaction, to 59°, and then it fell slowly and was kept at 40°. Over this period of time 4 more g of mercuric sulfate was added in portions. The reaction product was decanted with the catalyst; the main part of the methanol was evaporated over a water bath in a low vacuum at 40°. The reaction product was carefully neutralized with soda, extracted with ether, washed with water, and dried with sodium sulfate. After the ether was distilled off and the product was vacuum distilled, 38.5 g of 5-methyl-1-methoxy-7-ethoxy-4-hepten-3-one (V) was obtained.

B. p. 108-109° at 2 mm, d_4^{20} 0.9613, n_D^{20} 1.4640, MR_D 57.40; calc. 55.83.

Found %: C 65.83. 65.57; H 10.27, 10.15. $C_{11}H_{20}O_3$. Calculated %: C 66.00; H 10.00.

Hydrogenation of 5-methyl-1-methoxy-7-ethoxy-4-hepten-3-one (V). 2.9 g of the freshly-distilled alkoxy ketone (V) was hydrogenated in 10 ml of ethanol in the presence of a platinum catalyst. 0.4 liter of hydrogen was taken up instead of the 0.348 liter which was calculated. 2.2 g 5-methyl-1-methoxy-7-ethoxy-heptan-3-one (VII) was obtained.

B. p. 98-99° at 2 mm, d_4^{20} 0.9302, n_D^{20} 1.4380; MR_D 57.01; calc. 56.30.

Found %: C 65.03, 65.32; H 11.03, 11.15. $C_{11}H_{22}O_3$. Calculated %: C 65.34; H 10.89.

Oxidation of 5-methyl-1-methoxy-7-ethoxy-4-hepten-3-one (V). 11 g of the ketone (V) was mixed with 200 ml of water, and 27 g of finely-ground potassium permanganate was added to the mixture, with constant stirring over the course of 5 hours; after the addition of the potassium permanganate, the reaction mixture was allowed to stand overnight. On the following day the product was filtered, the manganese dioxide was washed twice with hot water, the neutral product was extracted from the filtrate with ether, and the ether solution was dried with sodium sulfate and distilled. 1.3 g of methylethoxyethyl ketone with a boiling point of 145-147° at 680 mm, n_D^{20} 1.4096 was obtained. The 2,4-dinitrophenylhydrazone of the obtained ketone melted at 100-101° and did not give a depression upon being mixed with a known sample.

The aqueous solution of the organic acids was evaporated until dry over a water bath, the residue was acidified with concentrated hydrochloric acid, extracted with ether, and the ether solution was dried with sodium sulfate and vacuum distilled. The product was 3.7 g of β-methoxypropionic acid with a boiling point of 103-105° at 11 mm; 199-203° at 680 mm, n_D^{20} 1.4201.

The splitting off of methanol from 5-methyl-1-methoxy-7-ethoxy-4-hepten - 3-one (V). 22.5 g of the ketone (V), 0.005 g of pyrogallol, and 0.5 g of para-toluenesulfonic acid were heated for 20 minutes over a metallic bath at 100° and at a pressure of 25 mm. Then 13 g of a substance with a boiling point of 88-90° at a pressure of 7 mm was distilled off. After two distillations, 7 g of 5-methyl-7-ethoxy-1,4-heptadien- 3-one (IV) was obtained.

B. p. 71-72° at 2 mm, d_4^{20} 0.9285, n_D^{20} 1.4770, MR_D 51.17; calc. 49.10.

Found %: C 71.32, 71.02; H 9.93, 9.60. $C_{10}H_{16}O_2$. Calculated %: C 71.43; H 9.52.

The obtained dienone (IV) is a yellowish, mobile liquid with a characteristic odor. On standing without a stabilizer it quickly thickens, forming a transparent solid polymer that is light yellow in color.

Hydrogenation of 5-methyl-7-ethoxy-1,4-heptadien- 3-one (IV). 3.5 g of the freshly-distilled ketone was hydrogenated in 10 ml of ethanol in the presence of a platinum catalyst. The quantity of hydrogen taken up was 1.1 liter; 1 liter of hydrogen is required for the hydrogenation of two double bonds. 2.8 g of 5-methyl-7-ethoxy-heptan-3-one (VI) was obtained in the form of a colorless, mobile liquid with a pleasant odor.

B. p. 68-69° at 3 mm, d_4^{20} 0.8827, n_D^{20} 1.4310, MR_D 50.45; calc. 50.03.

Found %: C 69.19, 68.90; H 12.27, 12.00. $C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.63.

Dehydration of methyl-β-ethoxyethylvinylethinylcarbinol (II). A mixture of 149 g of the carbinol (II), 0.005 g of pyrogallol, and 149 g of 50% sulfuric acid was heated, with constant stirring, over a water bath at 60° for one hour and 20 minutes. At the beginning of the reaction, a rise in temperature was noted (up to 73°). The reaction product was extracted with ether, neutralized with soda, washed with water, dried with sodium sulfate, and vacuum distilled. 80 g of 2-β-ethoxyethyl-1,5-hexadien-3-yne (VIII) was obtained.

B. p. 67-69° at 4 mm, d_4^{20} 0.8636, n_D^{20} 1.4970, MR_D 50.82; calc. 47.09.

Found %: C 80.41, 79.45; H 9.63, 9.33. $C_{10}H_{14}O$. Calculated %: C 80.0; H 9.33.

The obtained dienyne (VIII) is a colorless, mobile liquid; upon standing without a stabilizer it quickly polymerizes, forming a thick, glass-like polymer that is yellow in color.

Hydrogenation of 2-β-Ethoxyethyl-1,5-hexadien-3-yne (VIII). 3.2 g of freshly distilled dienyne (VIII) was hydrogenated in the presence of a Pt catalyst in 10 ml of ethyl alcohol. 2.1 liters of hydrogen was absorbed instead of the calculated 2.048 liters. We isolated 2.3 g of 3-methyl-1-ethoxyheptane (IX) in the form of a colorless, transparent liquid with a pleasant odor.

B. p. 88° at 33 mm, d_4^{20} 0.7829, n_D^{20} 1.4130, MR_D 50.34; calc. 50.02.

Found %: C 76.17, 76.46; H 13.90, 13.94. $C_{10}H_{22}O$. Calculated %: C 75.95; H 13.92.

Hydration of 2-β-ethoxyethyl-1,5-hexadien-3-yne (VIII). 500 g of the dienyne (VIII), which had been stabilized with pyrogallol, was added by drops, with energetic stirring, to a boiling mixture of 2 g 90% methanol, 2 ml of concentrated sulfuric acid, and 136 g of mercuric sulfate. The reaction mixture was heated with stirring for 28 hours. In the course of this time, 36 additional g of mercuric sulfate was added to the mixture. The reaction product was filtered, the main part of the methanol was distilled off in a vacuum (70 mm) over a water bath at 45-50°. The residue was neutralized with soda, extracted with ether, washed with water, dried with sodium sulfate and vacuum distilled. 99 g of a mixture of the products of hydration was obtained; the mixture boiled between 110-128° at 6 mm. 79 g of the pure 5-methoxy- 2-β-ethoxyethyl-1-hexen - 3-one (XI) was isolated by means of repeated distillations.

B. p. 100-102° at 2 mm, d_4^{20} 0.9602, n_D^{20} 1.4550, MR_D 56.51; calc. 55.83.

Found %: C 65.55, 65.58; H 10.37, 10.29. $C_{11}H_{20}O_3$. Calculated %: C 66.00; H 10.00.

Hydrogenation of 5-methoxy-2-β-ethoxyethyl-1-hexen - 3-one (XI). 2.8 g of the freshly-distilled ketone was hydrogenated in 10 ml of ethyl alcohol in the presence of a platinum catalyst. 0.4 liter of hydrogen was taken up instead of the calculated 0.334 liter. 2.2 g of 5-methyl-2-methoxy-7-ethoxy-heptan - 4-one (XIII) was obtained.

B. p. 99-100° at 5 mm, d_4^{20} 0.9292, n_D^{20} 1.4366, MR_D 56.95; calc. 56.30.

Found %: C 65.48, 65.29; H 11.01, 11.31. $C_{11}H_{22}O_3$. Calculated %: C 65.35; H 10.89.

Oxidation of 5-methoxy-2-β-ethoxyethyl-1-hexen - 3-one (XI). 17 g of the ketone was mixed with 200 ml of water, and 43 g of finely-ground potassium permanganate was added over the course of 15 hours, with intense stirring and cooling with water. The manganese dioxide was filtered and washed twice with boiling water; from the filtrate, the neutralized product was extracted with ether, and dried with sodium sulfate. 2 g of the substance remained after the distilling off of the ether. The aqueous solution was evaporated over the water bath until dry, the residue of the salt was acidified with concentrated hydrochloric acid (13 ml), the organic acids were extracted with ether, dried with sodium sulfate, and vacuum distilled; there was 2.2 g of the first fraction boiling at 40-45° at 50 mm; the second fraction contained 5.1 g and boiled at 110-116° at 18 mm; there was 3 g of tarry residue.

The first fraction, which was formic acid (calomel test), after drying with roasted sodium sulfate, was distilled under normal pressure; b. p. 99-101° at 680 mm.

The second fraction is a mixture of β-methoxybutyric and β-ethoxypropionic acids. They were distilled once more under normal pressure; two new fractions were obtained. The first fraction is β-methoxybutyric acid with a b. p. of 200-203° at 670 mm, n_D^{20} 1.4205. Its silver salt was prepared.

Found %: Ag 48.45, 48.34. $C_5H_9O_3Ag$. Calculated %: Ag 48.0.

The second fraction was mainly β-ethoxypropionic acid with b. p. 206-209° at 670 mm, n_D^{20} 1.4625. Its silver salt was obtained.

Found %: Ag 48.06. $C_5H_9O_3Ag$. Calculated %: Ag 48.0.

The splitting off of methanol from 5-methoxy-2-β-ethoxyethyl-1-hexen - 3-one (XI). 17 g of the alkoxy ketone (XI), which had been stabilized with pyrogallol, was vacuum distilled in the presence of 0.052 g para-toluenesulfonic acid. At first the mixture was heated for 20 minutes over a metallic bath at a temperature of 100° and a pressure of 30 mm; then 11.3 g of a substance with a b. p. of 93-97° at 5 mm, n_D^{20} 1.4737 was distilled off. After distillation 9 g of 2-β-ethoxyethyl-1,4-hexadien - 3-one (X) was obtained.

B. p. 81-82° at 2 mm, d_4^{20} 0.9547, n_D^{20} 1.4760, MR_D 49.65; calc. 49.10.

Found %: C 70.23, 70.19; H 9.83, 9.52. $C_{10}H_{16}O_2$. Calculated %: C 71.47; H 9.52.

Hydrogenation of 2-β-ethoxyethyl-1,4-hexadien- 3-one (X). 2.7 g of the ketone (b. p. 90-92° at 4 mm, n_D^{20} 1.4750) was hydrogenated in a solution of 10 ml of ethanol in the presence of a platinum catalyst. 0.8 liter of hydrogen was taken up; 0.76 liter is required for the hydrogenation of two double bonds. 1.8 g of 1-ethoxy-3-methyl heptan - 4-one (XII) was obtained.

B. p. 74-75° at 4 mm, d_4^{20} 0.8996, n_D^{20} 1.4345, MR_D 49.88; calc. 50.03.

Found %: C 69.39, 69.44; H 11.34, 11.45. $C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.62.

SUMMARY

Methyl-β-ethoxyvinylethinylcarbinol (II) was obtained by the action of magnesiumbromovinylacetylene on methyl-β-ethoxyethyl ketone (I); under the influence of mercuric sulfate in a methanol solution, the methyl-β-ethoxyvinylethinylcarbinol (II) is isomerized to the divinyl ketone (IV). The latter, under the conditions of the experiment, adds methanol and gives the dialkoxy ketone (V).

The vinylethinylcarbinol (II), upon heating with 50% sulfuric acid, was converted into the dienyne (VIII); this in turn, on being heated in 90% methanol in the presence of mercuric sulfate, is hydrated to the dienone (X). This dienone, under the conditions of the experiment, adds methanol and gives the dialkoxy ketone (XI). Upon the splitting off of methanol from the dialkoxy ketone through the use of para-toluenesulfonic acid, the dienone (X) is again obtained. On the oxidation of the dialkoxy ketone with potassium permanganate, formic, β-ethoxypropionic, and β-methoxybutyric acids are obtained; this confirms the structure of the dienyne (VIII) and the ketone (XI).

Hydrogenation has been carried out, and the hydrogenated derivatives of the above described unsaturated compounds have been obtained.

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THE OBTAINING OF SOME HALOGEN DERIVATIVES BY THE ADDITION OF A HYDROGEN HALIDE TO UNSATURATED COMPOUNDS

N. N. Lebedev

The addition of hydrogen chloride to the double bond is one of the well known reactions which is catalyzed by aluminum chloride. It has acquired special importance for the industrial synthesis of ethyl chloride [1]. However, there are a great many cases in which this reaction is not used, since many halogen derivatives, especially those having secondary and tertiary chlorine atoms, are unstable in regard to the action of aluminum chloride, which decomposes them, the hydrogen halide being split off [2]:

$$R'CHCl-CH_2R \xrightarrow{AlCl_3} R'CH=CHR + HCl.$$

The olefin, in its turn, may be further polymerized under the action of aluminum chloride.

Thermodynamic calculations show that the above described reaction does not have to go to the right at ordinary temperatures. The factor which causes the shifting of the equilibrium is probably the tendency of the aluminum chloride to form complexes with the unsaturated compounds. The olefin which is formed combines with the catalyst, which causes the continuous shifting of the reaction in the direction of the decomposition of the halogen derivative.

It was found that this undesired reaction could be avoided by using a nitrobenzene solution of aluminum chloride as a catalyst. In the complex [3]

$$[(C_6H_5NO_2)_2AlCl_2]^+ [AlCl_4]^-$$

which is formed in the solution, the aluminum chloride is sufficiently strongly linked with the nitrobenzene, and cannot form complexes with the olefins; therefore, the decomposition of the halogen derivatives cannot take place in this case. Thus, we found that ethylidene chloride and methyl chloroform were fully stable in a nitrobenzene solution of aluminum chloride, while the latter, in the pure form, decomposed them very violently, with the giving off of a great deal of heat, and the splitting off of a hydrogen halide.

This opens up the possibility of obtaining a wide group of halogen derivatives by the convenient method of adding a hydrogen halide to an olefin or an olefin chloride in a nitrobenzene solution of aluminum chloride.

$$CH_2=CCl_2 + HCl \xrightarrow[C_6H_5NO_2]{AlCl_3} CH_3CCl_3.$$

This method is not limited to chlorine derivatives; it was applied by us to bromine compounds

$$CH_3CH=CH_2 + HBr \xrightarrow[C_6H_5NO_2]{AlCl_3} CH_3CHBrCH_3.$$

It was established that in the case of the addition of hydrogen bromide, too, it is possible to use aluminum chloride as a catalyst; in this case, a mixture of halogen derivatives is not formed, since the aluminum bromide, which is formed by the equilibrium reaction

$$AlCl_3 + 3HBr \rightleftharpoons AlBr_3 + 3HCl,$$

immediately reacts with the chlorine derivative which is formed, replacing the halogen atom:

$$3RCHClCH_3 + AlBr_3 \rightarrow 3RCHBrCH_3 + AlCl_3.$$

It should be pointed out that the method proposed by us almost completely excludes the possibility of the polymerization of the olefin, since a nitrobenzene solution of aluminum chloride at room temperature does not show polymerizing action on such substances as propylene and n-butylene.

There are analogous advantages in the method of the addition of hydrogen halides to olefins, based on the use of an ether solution of aluminum chloride [4]; it is desirable to use this method for obtaining of compounds with high boiling points, which are difficult to separate from nitrobenzene by distillation.

The following compounds were obtained by the method described above: ethylidene chloride (56-58°, d_4^{20} 1.1750, n_D^{20} 1.4166) from vinyl chloride, with a yield of 85%; methyl chloroform (73-75°, d_4^{20} 1.3162, n_D^{20} 1.4194) from vinylidene chloride, with a yield of 75%; isopropyl chloride (36-37°, d_4^{20} 0.8610, n_D^{20} 1.3782) from propylene, with a yield of 60%; isopropyl bromide (58-60°, d_4^{20} 1.3145, n_D^{20} 1.4250) from propylene and HBr, with a yield of 70%; 1,2-dichloropropane (96-98°, d_4^{20} 1.1561, n_D^{20} 1.4395) from allyl chloride, with a yield of 65%; 1,2-dibromopropane (139-142°, d_4^{20} 1.9310) from allyl bromide and, HBr with a yield of 60%; sec-butyl chloride (67-69°, d_4^{20} 0.8721, n_D^{20} 1.3966) from n-butylene, with a yield of 70%.

In all cases the addition of the hydrogen halide was carried out in accordance with Markovnikov's rule.

EXPERIMENTAL

The method of carrying out the syntheses is given below; the preparation of ethylidene chloride and methyl chloroform are given as examples.

The preparation of ethylidene chloride. The apparatus for the preparation of ethylidene chloride consists of a flask, or better still, of a column, with a bubbler and a reflux condenser. 50 ml of a 10% solution of aluminum chloride in nitrobenzene is poured into the flask; during the reaction it is cooled with a water bath. Vinyl chloride and hydrogen chloride are passed separately through rheometers, mixed in a T-pipe, passed through a drying column containing roasted calcium chloride, and through a safety flask, and enter the reaction vessel through the bubbler. The speed of the gas is regulated by the rheometer in such a way that a 5-10% excess of hydrogen chloride is supplied. In order to observe the course of the reaction, it is desirable to place (after a safety flask) a Drexel bottle at the outlet of the reflux condenser. The speed of the vinyl chloride is regulated in this case in such a way that only individual rare bubbles of the gas pass through this bottle. After the end of the reaction process, the liquid is decomposed with dilute hydrochloric acid in a separatory funnel and washed with water. Further separation of the product may be carried out in two ways: 1) by steam distillation, separation from the water, drying with calcium chloride, and final distillation; 2) drying with calcium chloride, distillation of the product until the temperature of the vapor is 120°, and final distillation.

The final result in both cases is the gathering of a fraction boiling at 56-58°. From one mole of vinyl chloride, 80-85 g of ethylidene chloride (up to 85%) was obtained.

Isopropyl chloride and bromide, and sec-butyl chloride were obtained by the same method.

The preparation of methyl chloroform. The apparatus for the preparation of methyl chloroform consists of a flask with a bubbler, a reflux condenser, and a dropping funnel. The flask is placed in a cold water bath, and is charged with 50 ml of a 10% solution of aluminum chloride in nitrobenzene. The air is forced out of the apparatus with dry hydrogen chloride, and 67 g of vinylidene chloride, which has been previously dried, is added by drops from the funnel, the hydrogen chloride being passed through at the same time. The rate of the gas flow was regulated in such a way that the passage of the gas from the apparatus was insignificant.

The reaction was completed when, after all the vinylidene chloride had been added, no more hydrogen chloride was absorbed. The separation of the product was carried out as in the preceding example. A final fraction, boiling at 73-75° was collected. The yield was 100 g (75%).

SUMMARY

1. It has been found that nitrobenzene complexes of aluminum chloride are not capable of decomposing halogen derivatives into olefins and hydrogen halides.

2. This made possible the proposing of a new method for the obtaining of certain halogen derivatives by the addition of hydrogen halides to olefins or chloro.olefins, under the catalytic action of a solution of aluminum chloride in nitrobenzene.

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CATALYTIC TRANSFORMATIONS OF THE HALOGEN DERIVATIVES OF THE AROMATIC SERIES

III. THE MECHANISM OF THE ISOMERIZATION OF THE MONO-HALOGEN DERIVATIVES OF NAPHTHALENE

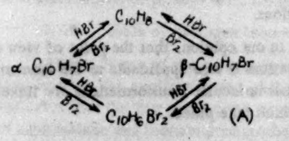
N. N. Vorozhtsov and N. M. Przhiyalgovskaya

It was shown earlier by one of us and A. M. Beskin [1], that the isomerization of monochloronaphthalenes by aluminum oxide in the presence of hydrogen chloride is a reversible process, which takes place without the noticeable formation of any by-products:

$$\alpha\text{-}C_{10}H_7Cl \xrightleftharpoons[400^\circ]{Al_2O_3,\ HCl} \beta\text{-}C_{10}H_7Cl.$$

Unlike the monochloronaphthalenes, the reversible isomerization of monobromonaphthalenes in the presence of the halogen salts of iron and hydrogen bromide, is always accompanied by the formation of considerable quantities of naphthalene and dibromonaphthalenes. In the opinion of some Dutch investigators [2], the isomerization of monobromonaphthalenes is caused by the reversibility of the process of bromination. The equilibrium between the isomers is established indirectly through the formation of napththalene and bromine according to scheme A.

It was established by us that catalytic isomerization of monobromonaphthalenes by aluminum oxide in the presence of hydrogen bromide, is also accompanied by the formation of naphthalene and dibromonaphthalenes. However, the data obtained by us on the study of the isomerization of monobromonaphthalenes shows that the intermolecular mechanism shown above cannot explain all the peculiarities of this process.



Thus, on the carrying out of the isomerization of monobromonaphthalenes in the presence of benzene, one of the products of the reaction is bromobenzene. If we assume only the intermolecular mechanism of the transformation of one isomer into the other, then the addition of benzene should lessen the degree of isomerization, since part of the bromine is combined with benzene in the form of bromobenzene.

Our experiments showed thaton the increasing of the molecular ratio of benzene to 1-bromonaphthalene, the quantity of the naphthalene in the reaction product rises greatly (up to 59% with 6.3 moles of benzene to 1 mole of bromonaphthalene), but that the content of the 2-isomer in the fraction of nonobromonaphthalenes was decreased practically not at all, and constituted 56% of the total.

The addition of benzene in the isomerization of chloronaphthalene in the presence of hydrogen chloride does not influence the course of the process in any way, since the reaction of the chlorination of naphthalene at 350° is practically not reversible.

Experiments on the isomerization of 1-bromonaphthalene by aluminum oxide in a stream of hydrogen fluoride also indicate that there is no dependence between the degree of isomerization and the quantity of naphthalene formed. At 250°, the isomerization of 1-bromonaphthalene reached 54.5%, practically no naphthalene being formed (3.3% naphthalene in all). Hydrogen bromide was discovered in the gases escaping from the reaction tube. Investigation of the reaction product showed that in this case there was no exchange reaction between bromine and fluorine [3], and therefore, the formation of hydrogen bromide can be explained only by the partial pyrolysis of bromonaphthalene. The presence in the system of a small quantity of hydrogen bromide also caused, evidently, a correspondingly small disproportionation.

The raising of the temperature to 550° in the isomerization of 1-chloronaphthalene in the presence of hydrogen chloride, led to the formation of naphthalene in this case too (29.4%). The content of the 2-isomer in the fraction of monochloronaphthalenes was 52.5%.

The formation of the naphthalene was evidently caused by the fact that at high temperatures, with a catalyst, the reaction of the chlorination of naphthalene becomes reversible:

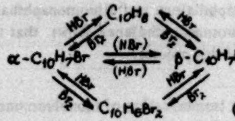
$$C_{10}H_7Cl + HCl \xrightarrow[550^\circ]{Al_2O_3} C_{10}H_8 + Cl_2.$$

The absence of dichloronaphthalenes in the reaction product can be explained by their decomposition, as a consequence of the high temperature of the experiment (550°). It is known that some dichloronaphthalenes are decomposed even at their boiling points (~ 300°).

All of the facts given above can be explained by the fact that the isomerization of both chloro- and bromonaphthalenes, in the presence of halogen halides and aluminum oxide, in the gaseous phase, takes place according to an intramolecular mechanism. Along with isomerization in the strict sense, intermolecular transformation of one isomer into another is also possible, with the intermediate formation of the naphthalene and the halide, as a consequence of the reversible character of the halogenation reaction. This transformation takes place only on the appearance of the reducing properties of the hydrogen halide, in the presence of which the isomerization is carried out.

In connection with this, the scheme proposed by the Dutch writers does not fully reflect the isomeric transformations of the bromonaphthalenes in the presence of hydrogen bromide. A new scheme (B) was proposed by us for this case; it includes both the intramolecular and the intermolecular transformations of the monobromonaphthalenes.

The data obtained by Brezhneva and Roginsky [4], on the investigation of the isomerization of monobromonaphthalenes in the presence of $AlBr_3$ containing a radioactive bromine atom, also indicates the intramolecular mechanism of the reaction.



(B)

(Catalyst: $FeCl_3$, Al_2O_3).

The proposed dual mechanism of the isomerization of chloro- and bromonaphthalenes is not unique. The isomerization of naphthalene sulfonic acid [5, 6] evidently takes place in an analogous manner.

In connection with the above, it is necessary to point out that Favorsky [7], on the basis of an enormous amount of experimental data, came to the conclusion that isomeric transformations in the aliphatic series are intramolecular reactions.

Our investigations show, in our opinion, that the point of view of Favorsky on isomeric transformations is also applicable to the isomerization of naphthalene derivatives. Intermolecular transformations are linked only with the subsidiary processes which take place.

EXPERIMENTAL*

The interaction of 1-chloro- or 1-bromonaphthalenes with hydrogen chloride or hydrogen bromide, in the presence of benzene.

The experiments were conducted at 350° over aluminum oxide. The speed of input of the solution of the naphthalene halide into the benzene was 5-6 ml/hour, that of the hydrogen halide was 55 ml/minute. The results of the experiments are given in Table 1. For comparison, the quantity of naphthalene formed in the absence of benzene is also given here.

Upon the distillation of the products of catalysis of reactions I, II and III, carried out in the presence of benzene, fractions with a boiling point of 152-154° and n_D^{20} 1.5594 were isolated in all three cases. The data given in the literature for bromobenzene are: boiling point 156.2° and n_D^{20} 1.5604 [8]. For identification the product was nitrated with nitric acid to the dinitro derivative. After recrystallization from dilute ethanol, yellow crystals were obtained in the form of small needles with a melting point of 72-73°. The literature data for 2,4-dinitrobromobenzene gives a melting point of 73°. After the determination of the melting point, a mixture test was carried out with known 2,4-dinitrobromobenzene; no depression of the melting point was observed. Thus, one of the products of reactions I, II and III is bromobenzene.

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* The apparatus and the method of work have been described in the previous communication [3].

TABLE 1

Reaction	I α-$C_{10}H_7Br$ + + HBr	II α-$C_{10}H_7Br$ + + HCl	III α-$C_{10}H_7Cl$ + + HBr	IV α-$C_{10}H_7Cl$ + + HCl
Quantity of naphthalene in the absence of benzene (in mole %)	20.8	22.4	22.1	0
Quantity of naphthalene in the presence of 2.5 moles of benzene per 1 mole of the naphthalene halide	39.9	26.4	38.8	0

TABLE 2

Number of moles of benzene per 1 mole of 1-bromonaphthalene	Quantity of naphthalene formed (in mole %)	Fraction of monobromonapthalenes	
		Solidification point	Content of the 2-isomer (in weight %)
0	20.8	19.1°	56.2
2.5	39.9	18.9	56.0
4.3	52.2	18.4	55.5
6.3	59.0	18.7	55.7

The influence of the ratio of benzene to 1-bromonaphthalene on the reaction of isomerization of 1-bromonaphthalene, in the presence of hydrogen bromide. The experiments were carried out at a temperature of 350° over aluminum oxide. Each experiment was continued for 3 hours. The speed of input of the bromonapthalene solution in benzene was 5-6 ml/hour, the speed of HBr – 55 ml/ minute. The results of the experiments are given in Table 2.

The interaction of 1-bromonaphthalene with hydrogen fluoride. The experiment was carried out at 250°. 3.53 g (0.170 mole) of 1-bromonaphthalene and 30 g (1.5 mole) of hydrogen fluoride were passed through aluminum oxide for three hours. The product of catalysis was washed, and subjected to fractionation (25.68 g) at atmospheric pressure. The following fractions were collected: the first with a b. p. of 215-220°, 0.46 g, freezing point, 49.5°; second b. p. 220-275°, 0.54 g, freezing point 34.2°; the third, b. p. 275-282°, 18.10 g, freezing point 17.1°; the fourth, b. p. 282-285°, 2.6 g; the residue 2.9 g.

0.004 mole of hydrogen bromide was found in the gases escaping from the reaction tube.

About 70 mg of the substances of the first and second fractions was melted with metallic potassium in a steel bomb. The qualitative test of the melt with zirconium chloride for fluorine [9], gave negative results. This indicates that the first and second fractions are, as is usual on the isomerization of 1-bromonaphthalene, mixtures of naphthalene and monobromonaphthalenes. The quantity of naphthalene formed is 0.73 g (0.0058 mole), or 3.34% of the number of moles of 1-bromonaphthalene originally passed over the aluminum oxide.

According to the freezing point, the third fraction contains 54% 2-bromonaphthalene.

Isomerization of 1-chloronaphthalene over aluminum silicate in a stream of hydrogen chloride at 550°. The experiment was carried out at 550° and the speed of the hydrogen chloride was 60 ml/minute. 18 g (0.11 mole) of 1-chloronaphthalene was passed through for three hours. The product of catalysis (14.23 g) was a solid substance, lemon-yellow in color. On distillation 12.8 g of the following fractions was collected; the first had a b. p. of 217-225°, 2.4 g, freezing point 76.3°; the second has a b. p. of 225-255°, 3.45 g, freezing point 42.1°; the third, b. p. 255-260°, 5.41 g, freezing point 20.1°; there was 0.9 g of residue.

The first fraction was naphthalene. The quantity of naphthalene formed was 4.16 g (0.0325 mole) or 29.4% of the number of moles of 1-chloronaphthalene originally passed through. The third fraction contained 52.5% 2-chloronaphthalene.

In the course of the experiment, the uncondensed gases, escaping from the receptacle for the products of catalysis, were collected with a 4% aqueous solution of potassium iodide in two successive, connected bottles. In the first bottle the solution became dark red. It was established by iodometric means that in the course of the experiment, 0.00204 mole of chlorine was given off.

SUMMARY

1. The isomerization of chloro- and bromonapthalenes (in the gaseous phase) over aluminum oxide, in the presence of hydrogen halides (HF, HCl, HBr) has been studied.

2. It has been shown that the isomerization of both the chloro- and bromonapthalenes takes place by an intramolecular mechanism. Along with the normal isomerization, under these given conditions it is also possible to have the intermolecular transformation of one isomer into another, with the intermediate formation of naphthalene and a halide, as a consequence of the reversible character of the reaction of halogenation.

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INVESTIGATIONS IN THE FIELD OF MOLECULAR CHROMATOGRAPHY

1. SEPARATION OF MIXTURES OF NITROPHENOLS

K. A. Ogloblin and G. V. Markina

There is very little literature data on the chromatographic separation of mixtures of nitrophenols.

On the separation of mixtures of the three isomeric mononitrophenols from benzene over calcium carbonate (they were passed over twice), Karrer and Nielsen found, that the adsorbability of the compounds falls in the series para-nitrophenol, meta-nitrophenol, and ortho-nitrophenol in that order [1]. The order of the adsorption, on polar adsorbents, of nitrophenols and other compounds, was set down in a short communication by Arnold [2]; he reported that this order depended on the size and number of the separate dipoles in the molecule. On the carrying out of chromatographic investigations of many nitro derivatives of the aromatic series from mixtures of petroleum ether with benzene and acetone, on silica gel mixed with celite, Ovenston established the place of some nitrophenol compounds in the adsorption series of the various nitro derivatives [4]. The literature data on the quantitative chromatographic separation of mixtures of nitrophenols is limited to the work by Norvall and Kenyon on the separation of two binary mixtures (para-nitrophenol with 2,6-dinitro-o-cresol and with 2,4-dinitro-α-naphthol) from ether over aluminum oxide (3).

From the available literature data, it is difficult to get an idea of the connection between the structure and physical-chemical properties of the nitrophenols, and their behavior under the conditions of chromatographic separation. But the establishment of such a dependence is a necessary condition for the rational utilization of the chromatographic method.

The order of adsorption of mixtures of substances depends on many factors, including the structure and properties of the compounds, the chemical nature and properties of the adsorbent, and the properties of the solvent used. In spite of this, it is possible to assume that under certain definite conditions the predominate influence of some factors will be observed, and that with a change in conditions, other factors will exert the main influence. An example of this is the known phenomenon of the change in the order of the adsorption of mixtures of substances, on the very same adsorbent, with a change in solvents [5]. Starting from this fact, it is impossible to consider correct that point of view which considers one of the factors, regardless of the concrete conditions, responsible for the order of the adsorption of mixtures; therefore, it is impossible to agree with Arnold's opinion [2], which recognizes the importance of the dipole and denies the importance of the acidity and basicity of the compounds, without taking into account the concrete conditions of the experiment.

On undertaking the investigation of the series of mixtures, we set as our goal the finding of the optimal conditions for their separation, and the discovery of those physico-chemical properties of the compounds, which, in the given concrete conditions, determined the order of their adsorption.

In the present communication are contained the results of work on the chromatographic separation of artificial mixtures of nitrophenols from non-polar solvents, or from solvents with a small degree of polarity, over aqueous aluminum oxide.

The following artificial mixtures of nitrophenols were taken for separation: 1) ortho-nitrophenol, meta-nitrophenol, para-nitrophenol, and 2,4-dinitrophenol in benzene, the developer – benzene; and 2) 2,4-dinitrophenol, 2,5-dinitrophenol, and 2,6-dinitrophenol in benzene, the developer – benzene and its mixture with ether.

For the separation, a commercial preparation of aluminum oxide which had been previously moistened, was used. Commercial aluminum oxide has an exceptionally great adsorption capacity for nitrophenol, as a consequence of which the chromatogram for such an oxide is a series of stably fixed, narrow adjoining zones, which makes the separation much more difficult. The most satisfactory results were obtained for aluminum which contained 14.3-15.5% water (desiccation at 110-115°) i.e. on the adsorbent with a greater moisture content than any of those prepared by Brochmann [6]. The chromatographic analysis was carried out under a small excess of pressure. Observation of the course of the separation was by visual means, since all the nitrophenols were colored. On washing with a solvent, part of the nitrophenols were washed out in the filtrate and those remaining in the column were extracted with a mixture of benzene and hydrochloric acid (see the experimental section of this paper).

Under the conditions of the experiment, both mixtures were fully divided into their component parts, the first mixture, after one passage through the column.

The results obtained in our experiments make it possible to arrange the nitrophenols in the following adsorption series (in order of increasing adsorbability):

For mixtures of four nitrophenols –

$$o\text{-}C_6H_4(OH)NO_2 < m\text{-}C_6H_4(OH)NO_2 < p\text{-}C_6H_4(OH)NO_2 < 2{,}4\text{-}C_6H_4(OH)(NO_2)_2;$$

For mixtures of three dinitrophenols –

$$2{,}5\text{-}C_6H_3OH(NO_2)_2 < 2{,}4\text{-}C_6H_3OH(NO_2)_2 < 2{,}6\text{-}C_6H_3OH(NO_2)_2.$$

In the evaluation of the results obtained, we took into account a number of factors. First of all, the experiment showed that nitrophenols are exceptionally stably held by aluminum oxide, and that it is very difficult to wash them out of the column with non-polar (benzene) or slightly polar (ethyl ether) solvents. An exception to this rule, to a certain extent, is ortho-nitrophenol; this difference is evidently linked with the presence in this compound of a strong, intramolecular hydrogen bond, which brings about its increased solubility. At the same time, the dinitrophenols are so firmly held by the aluminum oxide that they are not washed out fully even with ethyl alcohol. In addition, our attention is attracted by the considerably brighter color of the nitrophenols in the column compared to their color in the free state. We should also keep in mind the acid character of the nitrophenols and the possibility of the manifestation of the basic properties of aqueous aluminum oxide.

All this compels us to assume that under our conditions of the separation of the mixtures, the chemical interaction of the nitrophenols with aluminum oxide exerts a considerable influence on the order of adsorption. In accordance with this, the order of the adsorption of nitrophenols over aqueous aluminum oxide should be determined, mainly, by the degree of their acidity, i.e., the adsorbability of the nitrophenols should change parallel with their dissociation constants. In Table 1 are given the values of the dissociation constants and the order of adsorption of the nitrophenols, found by us on the separation of mixtures of four nitrophenols.

TABLE 1

Name of the compound	Distribution in the column (from the bottom up)	Dissociation constants [7]
Ortho-nitrophenol	I	$7.5 \cdot 10^{-8}$ (25°)
Meta-nitrophenol	II	$1.0 \cdot 10^{-8}$ (25°)
Para-nitrophenol	III	$9.6 \cdot 10^{-8}$ (25°)
2,4-Dinitrophenol	IV	$1.0 \cdot 10^{-4}$ (25°)

TABLE 2

Name of the compound	Distribution in the column (from the bottom up)	Dissociation constants [7]
2,5-Dinitrophenol	I	$7.0 \cdot 10^{-6}$ (25°)
2,4-Dinitrophenol	II	$1.0 \cdot 10^{-4}$ (25°)
2,6-Dinitrophenol	III	$2.0 \cdot 10^{-4}$ (25°)

As is evident from the data of Table 1, the order of distribution of the nitrophenols in the column, on the separation of mixtures of them from non-polar solvents, over aqueous aluminum oxide, is in correspondence with the order of the changes in the values of the dissociation constants. The anomalous position of ortho-nitrophenol shows precisely that the degree of acidity of the nitrophenols is only one of the factors which acts along with the other factors such as, the solubility, polarity, tendency toward the formation of hydrogen bonds with hydrated surfaces of the absorbent, etc.

On the chromatographic analysis of the mixture of the three dinitrophenols, the lowest in the column was 2,5-dinitrophenol and the highest was 2,6-dinitrophenol, i.e., the order of adsorption in this case corresponded with the order of the change in the dissociation constants (Table 2).

The correspondence in the values of the dissociation constants of the nitrophenols is reflected on the chromatograms obtained in our experiments in such a way that between the zones of the compounds with strongly differing constants, narrow "empty" zones appeared after development (para-nitrophenol and 2,4-dinitrophenol); at the same time, nitrophenols with dissociation constant values that were close to each other formed adjoining zones (para-nitrophenol and meta-nitrophenol, 2,4- and 2,6-dinitrophenol). In the latter case, quicker separation was possible through the use of mixtures of benzene and ether for washing.

In conclusion, it should be pointed out that aqueous solutions of aluminum oxide can be used for the separation of mixtures of nitrophenols of any composition, since there are considerable differences in the dissociation constants of all nitrophenols. It is possible to suppose that, in general, on chromatographic analysis over aqueous aluminum oxide from non-polar or slightly polar solvents (benzene, ether), of mixtures of organic acids of one class, such as nitrophenols, nitraminic acids, nitrobenzoic acids, etc., the order of their adsorption will be determined, to a considerable extent, by their degree of acidity.

EXPERIMENTAL

The apparatus for the chromatographic separation consisted of a glass tube with an outlet pipe soldered in the upper part and a slightly drawn out lower end. The top of the tube was connected to a dropping funnel with a polished section or with a rubber stopper. A thick wad of glass wool was placed in the narrow lower part of the tube; a layer of the adsorbent was placed on the glass wool. The equal distribution of the adsorbent was achieved by tapping on the walls of the tube with a glass rod which was covered with a piece of rubber tubing, until the level of the adsorbent ceased to fall. A small piece of filter paper was placed over the layer of the adsorbent. The outlet pipes of the tube and the dropping funnel were connected through a T-pipe to a U-shaped mercury manometer and a three-liter buffer bottle, connected by a hose to a water faucet. The pressure in the buffer bottle and in the apparatus was built up and maintained at the desired level by the periodic opening of the water faucet.

"Aluminum oxide for chromatography", series no. 15, produced by the Stalin factory, was used in the experiments. The aluminum oxide had been previously moistened to the necessary percentage of moisture by the addition of the calculated quantity of distilled water. The mixture was shaken in a closed flask for 2 hours, after which the adsorbent was kept in the closed flask for 24 hours. Moistening the adsorbent in this way guaranteed the homogeneity of the adsorbent; this was evident from the chromatograms and from the analytical data on the percentage of moisture. The determination of the amount of moisture was carried out by means of the drying of a weighed portion of aluminum oxide until constant weight at 110-115°. In addition, the total percentage of water was determined by the roasting of the adsorbent at 550-600° for half an hour. As solvents for the preparation of the original mixtures, development, and the washing of substances out of the column, benzene (ordinary purification with sulfuric acid and distillation in a distillation column) and anhydrous ethyl ether were used.

On the washing of the column, part of the nitrophenols went out with the filtrate, and the most stably adsorbed nitrophenols were extracted from the adsorbent with hydrochloric acid. The differently colored zones of the adsorbent, which were extracted from the column, were shaken in a bottle with a ground glass stopper, with a mixture of benzene and dilute hydrochloric acid (acid with a specific gravity of 1.19 was diluted with an equal volume of water). After 3 or 4 such workings of the adsorbent, practically all of the adsorbed substance went over into the benzene solution; the nitrophenol was separated from the benzene by the vacuum distillation of the solvent. The obtained crystals were dried in a vacuum-desiccator over aluminum oxide, after which they were weighed, and their melting point was determined. Difference in the weight of the nitrophenol separated in this way to the quantity of it in the original mixture was considered the yield of the product. Although the substances in the column were usually fully separated, their yield, with rare exceptions, was always below 100%; this was because of losses due to the discarding of the intermediate zones (in the case of adjoining zones) and those that occurred during the extraction of the nitrophenols from the adsorbent.

Separation of the mixture of ortho-nitrophenol, meta-nitrophenol, para-nitrophenol, and 2,4-dinitrophenol over aluminum oxide. 25 ml of a benzene solution containing 0.10 g each of ortho-, meta-, and para-nitrophenol, and 2,4-dinitrophenol was chromatographically analyzed in a column containing aluminum oxide (the column was 452 by 13.5 mm). The loss in weight of the adsorbent on roasting to 550-600° was 20.65-20.66%; the loss on drying at 110-115° was 14.25-14.30%. 200 ml of benzene was used as the developer; the excess pressure was 100 mm; the temperature was 17°. As a result of washing with benzene the following fractions of the filtrate were obtained (according to the rate of flow): the first was a light yellow, from the wide (215 mm) yellow zone; light yellow crystals in the form of needles were separated; weight 0.06 g (60%)* m. p. 46.5-47°; in a mixture test with ortho-nitrophenol (m. p. 44.7-45.5°) the mixture had m.p. 45-45.5°; the second fraction was light yellow from the wide light yellow zone (240 mm); the weight of the light yellow crystals, 0.07 g (70%), m. p. 97.4-97.7°; the mixed sample with meta-nitrophenol (m. p. 97.2-97.7°) melted at 97.6-97.8°.

The rest of the components of the mixture remained in the column in the form of a series of colored zones (from bottom to top); greenish yellow, width 120 mm (third fraction); bright yellow, 53 mm, (fourth fraction).

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* The relatively low yield of ortho-nitrophenol is explained by losses on drying [8].

Between the third and fourth fractions there was a white space about 2-3 mm wide. The colored zones of the adsorbent were extracted from the column with a spatula, and the parts on the boundary lines were discarded. After the working of each of the zones with a mixture of benzene and hydrochloric acid, fractions of the following crystals were obtained: the third – light yellow, long plates, weight 0.10 g (100%), m. p. 113-114°, the mixed sample with para-nitrophenol (m. p. 113.5-114.5°) melted at 113.5-114.6°; the fourth fraction – light yellow needles, weight 0.09 g (90%), m. p. 114-114.5°, the mixed sample with 2,4-dinitrophenol (m. p. 113.6-114°) melted at 113.4-114.0°.

The separation of the mixture of 2,4-, 2,5-, and 2,6-dinitrophenol over aluminum oxide. 10 ml of a benzene solution containing 0.10 g each of 2,4-, 2,5-, and 2,6-dinitrophenol was chromatographically analyzed over a column containing aluminum oxide; the size of the column was 178 by 14 mm. The adsorbent was humidified aluminum oxide, the loss of weight on roasting (550-600°) was 21.97-22.00%, the loss on drying (110-115°) was 15.47-15.49%; 40 ml of benzene was used as the developer, then a mixture of benzene with ether was used (100:1) 10 ml, (100:5) 19 ml, (1:1) 60 ml; ether 120 ml. The excess pressure was 20 mm, the temperature was 18°. After washing with the solvents, the following fractions were obtained.

1) A yellow filtrate from the orange zone (80 mm). Reddish yellow crystals, weight 0.08 g (80%), m. p. 108.5-109.5°. After repeated chromatographic analysis over the same oxide, a narrow, bright red zone which was not investigated was separated; 20 ml of the solution was used, 32 ml of benzene was used as the developer, the column was 104 by 10 mm, the pressure was 40 mm, and the temperature was 19°. From the main orange zone 0.07 g (70%) of yellow crystals was isolated; m. p. 108.3-108.7°, mixed sample with 2,5-dinitrophenol (m. p. 104-106°) melted at 105.2-106°.

2) The greenish yellow zone of the column (25 mm). After extraction from the column and the working of the adsorbent with a mixture of benzene and hydrochloric acid, 0.06 g (60%) of greenish yellow plates and needles was isolated; m. p. 115-115.7°, the mixed sample with 2,4-dinitrophenol (m. p. 113.5-114°) melted at 115-115.5°.

3) 0.04 g of yellow crystals was extracted with benzene and hydrochloric acid from each of the adjoining light orange (15 mm) and bright yellow (31 mm) zones of the adsorbent; m. p. 57-58° and 54-55°, mixed samples with 2,6-dinitrophenol melted between 57 and 60°. The substance was purified chromatographically over the same oxide, from benzene (10 ml of the solution, developer 110 ml of benzene, size of column 123 by 10 mm, pressure 40 mm, and temperature 19°). The main bright orange zone of the adsorbent (22 mm) was separated from the two narrow strips corresponding to the border regions (the lower – yellow, 1.5 mm, the upper – muddy orange, 0.5 mm). 0.07 g (70%) of yellow crystals was extracted from the bright orange zone with benzene and hydrochloric acid; m. p. 60-60.5°, the mixed sample with 2,6-dinitrophenol (m. p. 61-61.5°) melted at 60.3-61.5°.

SUMMARY

1. Chromatographic separations have been carried out on mixtures of ortho-nitrophenol, meta-nitrophenol, and para-nitrophenol and 2,4-dinitrophenol, and on mixtures of 2,4-, 2,5-, and 2,6-dinitrophenols; the separations were conducted from benzene and ether, over aqueous aluminum oxide.

2. It has been established that the order of adsorption of the indicated nitrophenols from benzene and ether over aqueous aluminum oxide corresponds to the order of their dissociation constants.

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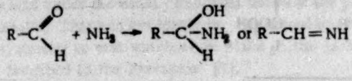
THE SYNTHESIS OF α-ALKYL-β-PHENYL-β, N-ALKYLAMINOPROPIONIC ACIDS AND SOME OF THEIR DERIVATIVES

V. M. Rodionov* and K. P. Preobrazhenskaya

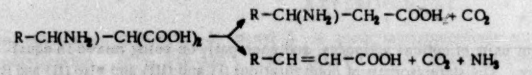
The purpose of the present work was the obtaining of C-alkylated and N-alkylated β-aminocarboxylic acids, and the comparison of their properties and transformations with β-amino acids which have a primary amine group. This work was undertaken in order to clarify the mechanism of the reaction of the formation of β-amino acids.

In the works of V. M. Rodionov and co-workers, two schemes of the formation of β-amino acids have been proposed; they may be represented in the following way:

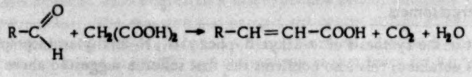
1)



$$R{-}CH{=}NH + CH_2(COOH)_2 \text{ — } R{-}CH(NH_2){-}CH(COOH)_2$$

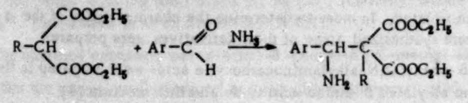


2)



$$R{-}CH{=}CH{-}COOH + NH_3 \rightarrow R{-}CH(NH_2){-}CH_2{-}COOH$$

The second scheme is less probable, since it has been shown in the work of Rodionov and Postovskaja [1] that the esters of mono-substituted malonic acid, under the conditions of the Rodionov reaction, give the esters of α-alkyl-β-aryl-β-aminoethane-α,α-dicarboxylic acids:

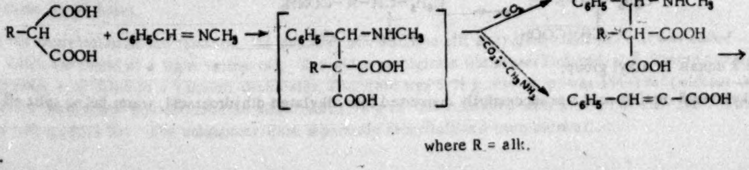


where R equals alkyl

and, as is evident, in this case α, β-unsaturated acids or their esters cannot be formed.

In favor of the first scheme there are many facts, which have been pointed out both in the works of the school of V. M. Rodionov [2, 3], and by some Soviet [4] and foreign [5] authors.

In order to confirm the first scheme of the mechanism of the reaction of the formation of β-amino acids and to prove that various substituted malonic acids are capable of being added to aldimines, we synthesized several α-alkyl-β-phenyl-β, N-alkylaminopropionic acids. This synthesis was accomplished by means of the interaction of alkylmalonic acids with benzalmethylamine, the readily accessible first representative of the aliphatic-aromatic aldimines:



where R = alk.

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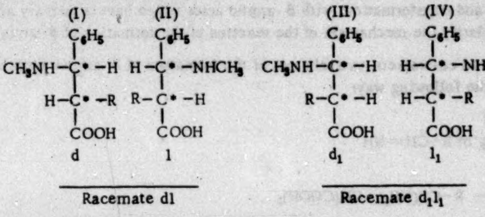
*Deceased.

The addition of the alkylmalonic acids (ethyl-, butyl-, and benzyl-) was carried out with complete success, which served as a new confirmation of the first scheme.

On the carrying out of these reactions, it was also established that, along with the formation of the alkylated β-amino acids, the corresponding unsaturated acids are always formed.

On the synthesis of α-alkyl-β-phenyl-β, N-alkylaminopropionic acids by the Rodionov reaction, acids with two asymmetrical carbon atoms were obtained. Consequently, one may expect four optically active forms, and, therefore, two racemates.



where R equals an alkyl group.

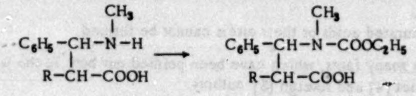
Thus, we must have here two different pairs of optical antipodes, and each pair, on being mixed in equal quantities, should give an inactive substance. The stereoisomers of configurations (I) and (III) and also (II) and (IV), while they are not antipodes, turn out to be diastereoisomers.

And, actually, it was established by us that on the synthesis of α-alkyl-β-phenyl-β, N-methylaminopropionic acids, two acids (two diastereoisomers) are always obtained; this also confirms the first scheme suggested above.

The separation of the two diastereoisomeric forms was accomplished by means of fractional crystallization from alcohol.

Further reactions for α-ethyl-β-phenyl-β, N-methylaminopropionic, α-N-butyl-β-phenyl-β-N-methylaminopropionic, and α-benzyl-β-benzyl-β-phenyl-α-Nmethylaminopropionic acids have been carried out so far with only one of the diastereoisomeric forms which have been isolated. In order to determine the characteristics of the α-alkyl-β-phenyl-β,N-alkylaminopropionic acids which were synthesized, some of their derivatives were prepared.

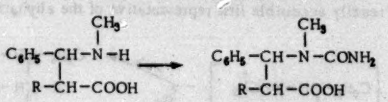
1. The carboethoxy derivatives of α-alkyl-β-phenyl-β,N-alkylaminocarboxylic acids were prepared in the usual way by the action of the chlorocarbonic ester on the alkylated β-amino acid in an alkaline medium [6].



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{C_6H_5-CH-N-H}\\ |\\ \mathrm{R-CH-COOH}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{C_6H_5-CH-N-COOC_2H_5}\\ |\\ \mathrm{R-CH-COOH}\end{array}$$

Where R equals H, alkyl group.

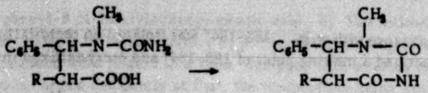
2. Some alkylated β-ureido-acids were also prepared, since, as is known, they are very characteristic compounds for amino acids and are often used for the identification of the latter.



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{C_6H_5-CH-N-H}\\ |\\ \mathrm{R-CH-COOH}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{C_6H_5-CH-N-CONH_2}\\ |\\ \mathrm{R-CH-COOH}\end{array}$$

Where R equals H, alkyl group.

3. Alkylated β-ureido acid was successfully converted into alkylated dihydrouracil, water being split off in the process.



$$C_6H_5-\underset{\displaystyle R-CH-COOH}{CH}-\overset{\displaystyle CH_3}{N}-CONH_2 \longrightarrow C_6H_5-\underset{\displaystyle R-CH-CO-NH}{CH}-\overset{\displaystyle CH_3}{N}-CO$$

Where R equals H, alkyl group.

On the closing of β-phenyl-β, N-1-methylureidopropionic acid, 3-N-methyl-4-phenyldihydrouracil was definitely obtained; this was fully confirmed by the analysis of this substance. However, it melted at 164-165°, and not at 158-159.5°, as was indicated by Evans and Johnson [5] who were the first to obtain it.

The obtaining of carboethoxy derivatives, β-ureido acids, and dihydrouracils for alkylated β-aminocarboxylic acids, takes place analogously to the process involved for β-amino acids which contain a primary amino group.

It is necessary to point out that β-phenyl-β, N-benzylaminopropionic acid differs in a number of its chemical properties from the other alkylated β-amino acids.

Thus, attempts to prepare the carboethoxy derivative and the β-ureido acid for β-phenyl-β, N-benzylaminopropionic acid under the usual conditions used for the preparation of the derivatives of β-amino acids did not give positive results. This can evidently be explained by the fact that the accumulation of phenyl groups causes steric hindrance, similar to that which takes place in the case of the closing of ω-arylsubstituted ureido acids, which has been described in the literature [7].

EXPERIMENTAL

The preparation of α-ethyl-β-phenyl-β, N methylaminopropionic acid. A mixture of 7.09 g (0.059 mole) benzalmethylamine (b. p. 179-180°), 7.55 g (0.057 mole) of ethylmalonic acid (m. p. 111.5-112°), and 40 ml of anhydrous benzene were heated in a three-necked bottle, equipped with a reflux condenser, a mechanical stirrer, and a thermometer. The reaction was carried out gently at first at 55-60° for 2 hours (at this temperature the main reaction of decarboxylation takes place); then the reaction mixture was kept at 60-70° for two hours, and finally, the temperature was raised to 80-85° and maintained at that level for 6 hours. On the completion of the heating, the benzene was distilled off and anhydrous ether was added to the residue. The white precipitate was filtered off, washed several times with anhydrous ether, and dried. The yield – 5.35 g (45%). After two recrystallizations from alcohol 2.6 g of the substance (22%) was separated; its m. p. was 205-206°.

4.16 mg sub.: 10.58 mg CO_2; 3.19 mg H_2O. 7.51 mg sub.: 19.08 mg CO_2; 5.74 mg H_2O. 7.95 mg sub.: 0.453 ml N_2 (22°, 752 mm). 5.33 mg sub.: 0.318 ml N_2 (23°, 752 mm). Found %: C 69.37, 69.20; H 8.58, 8.54; N 6.68, 6.81. $C_{12}H_{17}O_2N$. Calculated %: C 69.56; H 8.21; N 6.77.

The obtained substance was α-ethyl-β-phenyl-β, N-methyl-aminopropionic acid.

After the solvent was driven off and anhydrous ether was added, a second isomer of α-ethyl-β-phenyl-β, N-methyl-aminopropionic acid was isolated from the mother liquor. After recrystallization from ligroine, 1.11 g of a substance with a melting point of 170° was obtained. A mixed sample of the two diastereoisomers of α-ethyl-β-phenyl-β,N-methylaminopropionic acid melted at 156-160°. 3.1 g (30%) of α-ethylcinnamic acid with a melting point of 104° was obtained from the ether solution, after the driving off of the solvent and recrystallization from water (the literature data gives 104-105° as the melting point).

The preparation of α-n-butyl-β-phenyl-β, N-methylaminopropionic acid. 8.6 g (0.054 mole) of n-butylmalonic acid (m. p. 101°) was introduced into a solution of 7.6 g (0.063 mole) of benzalmethylamine in 40 ml of dry benzene.

The reaction was carried out in a three-necked bottle, equipped with a mechanical stirrer and a reflux condenser. The reaction mixture was heated at 60-70° for 2 hours, then the temperature was gently raised to 80-85° and held there for 10 hours.

On the completion of the reaction, the benzene was distilled off; anhydrous ether (50 ml) was added to the residue, which consisted of a light yellow oil. The white precipitate which was isolated, was filtered, washed with anhydrous ether, and dried in a vacuum-desiccator. The yield was 5.74 g, the m. p. was 174-175° (without decomposition). From the filtrate was obtained an additional 2.18 g of the substance with a m. p. of 190-192°. The total yield was 7.92 g (62.8 %). The substances were separately recrystallized from alcohol.

From the 5.74 g, 3.43 g (27%) of substance with m. p. 183-184° was isolated on recrystallization. After two recrystallizations from alcohol the product had a melting point of 183-184° and recrystallized in the form of small needles.

From the 2.18 g (m. p. 190-192°), 1.8 g of a substance with a m. p. of 200-201° was obtained after recrystallization from alcohol. After two recrystallizations from alcohol, the yield was 1.16 g, the m. p. was 205°; the substance crystallized in the form of fine needles. A mixed sample of the two diastereoisomers (m. p. 183-184° and m. p. 205°) melted at 172-174°.

Analysis of the substance with m. p. 183-184°.

5.20 mg sub.: 13.57 mg CO_2; 4.43 mg H_2O. 5.65 mg sub.: 14.78 mg CO_2; 4.84 mg H_2O. 8.21 mg sub.: 0.412 ml N_2 (19.5°, 755 mm). 5.38 mg sub.: 0.268 ml N_2 (19.5°, 755 mm). Found %: C 71.21, 71.39; H 9.53, 9.58; N 5.81, 5.77. $C_{14}H_{21}O_2N$. Calculated %: C 71.49; H 8.93; N 5.95.

The synthesized substance is α-n-butyl-β-phenyl-β,N-methylaminopropionic acid; it is quite soluble in alcohol, benzene, acetone, and is slightly soluble in ether.

The corresponding unsaturated acid was isolated from an ether solution in the usual way. After recrystallization from dilute alcohol, 2.7 g (25%) of α-n-butylcinnamic acid was obtained. The melting point was 83° (according to the literature data the m. p. is 83-84°).

The obtaining of α-benzyl-β-phenyl-β,N-methylaminopropionic acid. a) A mixture of 14.6 g (0.075 mole) of benzylmalonic acid (m. p. 117-118°) and 10.1 g (0.084 mole) of benzalmethylamine in 60 ml of dry benzene was heated in a bottle with a reflux condenser over a water bath for two hours at 65-70°; even at this temperature the reaction of decarboxylation took place to an appreciable extent. The temperature was gradually raised and was held at 85° for 10 hours; thereupon, white crystals were formed on the walls of the bottle, and near the end of the period of heating the entire contents of the bottle consisted of a solid, white crystalline mass. The precipitate was filtered and was washed several times with anhydrous ether in order to separate it fully from the unsaturated acid; after this it was dried. The yield was 13.0 g (64.2%), the m. p. was 198-202°. After two recrystallizations from methyl alcohol 6.13 g (30.3%) with a m. p. of 218-219° was obtained.

5.04 g of the substance (about 25%) was isolated from the mother liquor after the driving off of the excess solvent and the addition of ether. After recrystallization from dilute alcohol, the yield was 4.13 g (20.4%) of a white crystalline powder with a melting point of 188-189°. The mixed sample of the two diastereoisomers (melting points 218-219° and 188-189°) melted at 180-183°.

Analysis of the substance with m. p. 218-219°.

3.91 mg sub.: 10.84 mg CO_2; 2.57 mg H_2O. 3.88 mg sub.: 10.77 mg CO_2; 2.53 mg H_2O. 4.38 mg sub.: 0.214 ml N_2 (21°, 738 mm). 4.65 mg sub.: 0.224 ml N_2 (22°, 738 mm). Found %: C 75.61, 75.70; H 7.35, 7.29; N 5.50, 5.41. $C_{17}H_{19}O_2N$. Calculated %: C 75.83; H 7.06; N 5.20.

The substance obtained is α-benzyl-β-phenyl-β,N-methylaminopropionic acid.

After the driving off of the solvent from the ether solution the precipitate began to crystallize.

On recrystallization from benzene, 3.73 g (20.8%) of α-benzylcinnamic acid was obtained; m. p. 156-157° (literature data: m. p. 158°).

b) A mixture of 6.28 g (0.06 mole) of benzaldehyde, 9.7 g (0.05 mole) of benzylmalonic acid, 5.05 g (0.075 mole) of methylamine hydrochloride, and 7.5 g of dehydrated potassium acetate in 25 ml of glacial acetic acid was placed in a flask equipped with a reflux condenser, and heated over a water bath; first, the mixture was heated at 70-80° for 1 hour, then, it was heated over a boiling water bath for 10 hours. Carbon dioxide was given off from the mixture, which was homogeneous at first, and a crystalline substance was precipitated out. The thick crystalline mass which was obtained on the cooling of the reaction mixture was extracted with dilute hydrochloric acid. The filtrate, which had been acidified with hydrochloric acid, was first concentrated over the water bath and then extracted two or three times with ether; the aqueous solution was neutralized with a concentrated solution of sodium acetate. In order to obtain full crystallization of the precipitate, it was allowed to stand for 24 hours; then, it was separated, washed with water, and dried. The yield was 7.56 g (56.4%), the m. p. was 189-192°. After two recrystallizations from methyl alcohol, 3.7 g of a substance with a m. p. of 218-219° was obtained in the form of fine, colorless needles. The substance was α-benzyl-β-phenyl-β,N-methylaminopropionic acid; a mixed sample, made with this substance obtained by other means, did not give a depression of the freezing point.

Preparation of β-phenyl-β,N-benzylaminopropionic acid. a) The following components were taken in equimolecular quantities: 10.30 g of benzylamine (b. p. 185-187°), 10.46 g of benzaldehyde, 10.09 g malonic acid, and 55 ml of dry benzene were heated in a flask equipped with a reflux condenser, over a water bath. The heating of the mixture was carried out gently at first, the temperature being kept at 60-70° for 3 hours; thereupon, bubbles of carbon dioxide were given off; a large quantity of a white, flaky precipitate fell to the bottom of the flask. 15 ml more of dry benzene was added to the precipitate and the mixture was heated for eight hours at 80-85°.

On the completion of the reaction, the benzene was distilled off and anhydrous ether (80 ml) was added to the residue; on cooling and stirring, a white, fine, crystalline precipitate was obtained, which was filtered, washed several times with anhydrous ether, and dried. The yield was 13.18 g (54%), the m. p. was 177-178°. After recrystallization from methyl alcohol 9.45 g (38.5%) of a substance with a m. p. of 183-184° was obtained.

Analysis of the substance with m. p. 183-184°.

4.12 mg sub.: 11.40 mg CO_2; 2.39 mg H_2O. 4.67 mg sub.: 12.94 mg CO_2; 2.81 mg H_2O. 6.01 mg sub.: 0.270 ml N_2 (19.5°, 755 mm). 7.48 mg sub.: 0.345 ml N_2 (19.5°, 755 mm). Found %: C 75.50, 75.61; H 6.49, 6.73; N 5.21, 5.35. $C_{16}H_{17}O_2N$. Calculated %: C 75.37; H 6.66; N 5.49.

The synthesized substance is β-phenyl-β,N-benzylaminopropionic acid; it was crystallized from methyl alcohol in the form of fine, colorless, lustrous needles, which are slightly soluble in water, ether, and benzene, and quite soluble in methyl and ethyl alcohol.

4.3 g of cinnamic acid, with a m. p. of 133° was extracted from the ether solution after working in the usual way, and recrystallization from water. A mixture test with pure cinnamic acid did not give a depression of the melting point.

b) A mixture of 3.52 g (0.032 mole) of benzylamine, 3.5 g (0.033 mole) of benzaldehyde, 3.45 g (0.033 mole) of malonic acid, and 20 ml of dry benzene were gently heated in a flask with a descending condenser, over a water bath at 60,65° for 2.5 hours; toward the end, the temperature was raised and held for half an hour at 70°. Thereupon a large quantity of a white, flaky substance was precipitated out; the precipitate was separated, washed several times with anhydrous ether and dried. The yield was 60 g (61%) the m. p. was 127-129° (with decomposition).

After recrystallization from anhydrous alcohol at a temperature of 60-70°, 3.06 g (31%) of a substance with a m. p. of 138-140° was obtained.

4.71 mg sub.: 11.87 mg CO_2; 2.39 mg H_2O. 4.10 mg sub.: 10.31 mg CO_2; 2.12 mg H_2O. 4.76 mg sub.: 0.199 ml N_2 (25°, 754 mm). 5.98 mg sub.: 0.254 ml N_2 (25°, 754 mm). Found %: C 68.77, 68.72; H 5.68, 5.79; N 4.75, 4.83. $C_{17}H_{17}O_4N$. Calculated %: C 68.2; H 5.68; N 4.68.

The substance which was isolated was, evidently, an intermediate product which was formed on the interaction of benzylamine, benzaldehyde, and malonic acid; it was crystallized in the form of colorless, lustrous plates, which were difficultly soluble in water, ether, benzene, and cold alcohol, and quite soluble in hot alcohol.

The preparation of the carboethyoxy derivative of β-phenyl-β, N-methylaminopropionic acid. To 1.12 g (0.006 mole β-phenyl-β,N-methylaminopropionic acid with a m. p. of 168°, dissolved in 10 ml of a 109° solution of potassium hydroxide (three times as much), was added over a period of 20 minutes, with mechanical stirring and cooling down to 0°, 0.65 ml of the ethyl ester of chlorocarbonic acid (excess 10%).

The solution was mixed for 1 hour with cooling, then for one hour at room temperature. The solution was again cooled to 0° and acidified with hydrochloric acid (1: 1) until it gave an acid reaction on a Congo red indicator. First an oil precipitated, which began to crystallize in the form of course, white crystals; the latter were separated, washed, and dried. The yield was 1.01 g (64.3%) of a carboethoxy derivative with a m. p. of 76-78°. After recrystallization from a mixture of ether and petroleum ether 0.9 g of the carboethoxy derivative with a m. p. of 77-78° was isolated; it crystallized in the form of coarse plates.

6.16 mg sub.: 14.09 mg CO_2; 3.80 mg H_2O. 4.17 mg sub.: 9.52 mg CO_2; 2.59 mg H_2O. 7.71 mg sub.: 0 389 ml N_2 (20.5°, 752 mm). 6.18 mg sub.: 0.320 ml N_2 (20.5°, 752 mm). Found %: C 62.42, 62.30; H 6.90, 6.95, N 5.81, 5.96. $C_{13}H_{17}O_4N$. Calculated %: C 62.16; H 6.77; N 5.58.

The obtained compound is a carboethoxy derivative of β-phenyl β,N-methylaminopropionic acid; it is quite soluble in the ordinary organic solvents: ether, alcohol, benzene, acetone; it is less soluble in petroleum ether.

The obtaining of the carboethoxy derivative of α-ethyl-β-phenyl-β,N-methylaminopropionic acid. To 0.9 g (0.004 mole) of α-ethyl-β-phenyl-β,N-methylaminopropionic acid with a m. p. of 205-206° dissolved in 10 ml of a 10% solution of potassium hydroxide, was added gradually from a graduated pipet over the course of 20 minutes (with mechanical stirring and cooling of the solution to –1°), 0.46 ml of the ethyl ester of chlorocarbonic acid (10% excess). On the addition of the chlorocarbonic ester, the solution was mixed for an hour with cooling, and then, for one more hour, at room temperature. The solution was first cooled to 0° and acidified with hydrochloric acid (1: 1) until it showed an acid reaction with a Congo red indicator. An oil was precipitated, and on standing, began to crystallize. The yield was 0.97 g (80%); the m. p. was 114-117°. After recrystallization from a mixture of ether and petroleum ether, 0.9 g of a substance with a m. p. of 117-118° was obtained in the form of fine, colorless needles.

4.70 mg sub.: 11.12 mg CO_2; 3.20 mg H_2O. 6.39 mg sub.: 15.07 mg CO_2; 4.43 mg H_2O. 7.60 mg sub.: 0.331 ml N_2 (21.5°, 750 mm). 5.98 mg sub.: 0.266 ml N_2 (21.5°, 750 mm). Found %: C 64.56, 64.36; H 7.62, 7.75; N 4.98, 5.09. $C_{15}H_{21}O_4N$. Calculated %: C 64.51; H 7.53; N 5.02.

The obtained compound is a carboethoxy derivative of α-benzyl-β-phenyl-β,N-methylaminopropionic acid; it is quite soluble in alcohol, ether, benzene, and acetone, and slightly soluble in water and petroleum ether.

The preparation of the carboethoxy derivative of α-benzyl-β-phenyl-β,N-methylaminopropionic acid. In a three-necked bottle, equipped with a mechanical stirrer, a thermometer, and a graduated pipet, was placed 18 ml of a 10% solution of potassium hydroxide. 2.58 g of α-benzyl-β-phenyl-β,N-methylaminopropionic acid with a m. p. of 218° was added. The solution was cooled to –2°, and 1.0 ml of the ethyl ester of chlorocarbonic acid (10% excess) was added gradually over a period of 30 minutes, with constant stirring of the solution, and with the temperature kept in the interval from 0 to +3°. The mixing was continued for 1 hour with cooling of the solution, and then for 1.5 hours at room temperature. The solution was first cooled to 0° and gently acidified with hydrochloric acid (1: 1) until it gave an acid reaction with a Congo red indicator; the white residue, which was separated, was allowed to stand until the following day in order to achieve better crystallization. Then the precipitate was isolated, washed with a water, and dried. The yield was 3.07 g. After recrystallization from aqueous alcohol 2.85 g (87%) of a substance with a m. p. of 139-141° was obtained. After two recrystallizations from aqueous alcohol, the m. p. was 139.5-141°.

4.92 mg sub.: 12.67 mg CO_2; 2.90 mg H_2O. 4.54 mg sub.: 11.68 mg CO_2; 2.74 mg H_2O. 7.256 mg sub.: 0.260 ml N_2 (22°, 750 mm). 4.721 mg sub.: 0.159 ml N_2 (22°, 749 mm). Found %: C 70.27, 70.21; H 6.59, 6.75; N 4.09, 3.83. $C_{20}H_{23}O_4N$. Calculated %: C 70.38; H 6.74; N 4.10.

The synthesized substance is a carboethoxy derivative of α-benzyl-β-phenyl-β,N-methylaminopropionic acid; it is quite soluble in ether, benzene, and alcohol, and difficultly soluble in water and petroleum ether.

β-Phenyl-β,N-1-methylureidopropionic acid*. 1.37 g (0.007 mole) of β-phenyl-β,N-methylaminopropionic acid with a m. p. of 167-168°, 0.70 g of potassium cyanate, and 7.5 ml of water were heated in a flask equipped with a reflux condenser for 2.5 hours over a boiling water bath. On the completion of the heating, the solution was filtered in order to rid it of the small amount of impurities present, cooled to 0°, and gently acidified with hydrochloric acid (1: 1) until it gave an acid reaction to a Congo red indicator.

The white, flaky precipitate which was separated was allowed to stand for several hours, filtered, washed successively with water and ether, and dried. The yield was 1.13 g (66.5%) of β-phenyl-β N-methylureidopropionic acid with a m. p. of 165°. After recrystallization from alcohol the m. p. was 165-167° (Johnson gives m. p. 165-167°.

α-Ethyl-β-phenyl-β,N-1-methylureidopropionic acid. 0.8 g (0.0038 mole) of α-ethyl-β-phenyl-β, N-methylaminopropionic acid with a m. p. of 205-206°, 0.34 g of potassium cyanate (10% excess), and 10 ml of water were heated in a flask equipped with a reflux condenser for 2 hours and 40 minutes over a boiling water bath. On the completion of the heating, the solution was cooled, filtered to remove the small amount of admixtures, again cooled to 0° and acidified with hydrochloric acid (1: 1) until an acid reaction was given with Congo red indicator. The white, flaky precipitate which separated is allowed to stand until the next day for better crystallization, and then filtered, washed first with water, then with ether, and dried. The yield was 0.9 g (93%), the m. p. was 202°. After recrystallization from alcohol, 0.52 g (53.9%) of a substance with an m. p. of 208° was isolated. A mixed sample of the obtained substance with α-ethyl-β-phenyl-β,N-methylaminopropionic acid gave a depression of the melting point (m. p. 175-180°).

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* Obtained first by Evans and Johnson [5], but the conditions under which the experiment was carried out were not described in detail.

4.54 mg sub.: 0.423 ml N_2 (18.5°, 761 mm). 4.50 mg sub.: 0.422 ml N_2 (19°, 762 mm). Found %: N 10.88, 10.99. $C_{13}H_{18}O_3N_2$. Calculated %: N 11.20.

The synthesized substance is α-ethyl-β-phenyl-β,N-1-methylureidopropionic acid, which is crystallized in the form of fine, colorless needles, difficultly soluble in ether, benzene, and cold water, and quite soluble in alcohol.

α-n-Butyl-β-phenyl-β,N-1-methylureidopropionic acid. 1.0 g (0.004 mole) of α-n-butyl-β-phenyl-β,N-methylaminopropionic acid with a m. p. of 183°, 0.64 g (0.008 mole) of potassium isocyanate (excess 88%), and 10 ml of water were heated in a flask equipped with a reflux condenser for 4.5 hours over a boiling water bath. It should be pointed out that in the very first ten minutes of the heating the entire precipitate went into solution. On the completion of heating, the solution was cooled, filtered to remove the small quantity of impurities, again cooled to 0° and acidified with hydrochloric acid (1:1) until it gave an acid reaction with a Congo red indicator. The precipitate which was isolated was allowed to stand until the following day in order to improve the crystallization, then it was filtered, and washed several times with water and ether. The yield was 0.73 g, the m. p. was 205°. After two recrystallizations from alcohol, 0.58 g of a substance with m. p. of 213-214° was isolated; the yield was 74%, calculated on the butylamino acid which entered into the reaction. A mixed sample of the obtained substance with the original α-n-butyl-β-phenyl-β,N-methylaminopropionic acid gave a sharp depression of the melting point (m. p. 167-170°).

4.57 mg sub.: 0.401 ml N_2 (21.5°, 755 mm). 5.23 mg sub.: 0.467 ml N_2 (21.5°, 755 mm). Found %: N 10.10, 10.28. $C_{15}H_{22}O_3N_2$. Calculated %: N 10.07.

The synthesized substance is α-n-butyl-β-phenyl-β-N-1-methylureidopropionic acid. After acidification with hydrochloric acid, the solution was concentrated, and, on cooling, a 10% solution of potassium hydroxide was added; then the amino acid which had not entered into the reaction was precipitated with acetic acid. The white, flaky precipitate which was separated was filtered and washed with water and anhydrous ether.

After recrystallization from alcohol, 0.34 g of α-n-butyl-β-phenyl-β,N-methylaminopropionic acid with a m. p. of 182-183° was obtained. A mixed sample of this substance with pure α-n-butyl-β-phenyl-β,N-methylaminopropionic acid did not give a depression of the melting point.

3-N-methyl-4-phenyldihydrouracil*. 0.5 g (0.002 mole) of β-phenyl-β,N-1-methylureidopropionic acid (m. p. 165-167°) and 10 ml of 12% hydrochloric acid were boiled in a flask with a reflux condenser for two hours on a grid. On the completion of the heating, the solution was filtered and cooled; white, lustrous crystals were separated and filtered, washed with water, ether, and dried. The yield was 0.38 g (83%) of 3-N-methyl-4-phenyl-dihydrouracil with a m. p. of 163-164°.

After recrystallization from alcohol, 0.3 g of the dihydrouracil with a m. p. of 164-165° was isolated in the form of long, lustrous needles. After two recrystallizations from alcohol, the substance melted at 164-165°. A mixed sample of the obtained dihydrouracil with the original ureido acid had a melting point of 151-155°.

Since the m. p. of the 3-N-methyl-4-phenyldihydrouracil synthesized by Johnson differed from that obtained by us (Johnson gives 158-159.5°), a full analysis of the substance with a m. p. of 164-165° was carried out.

4.98 mg sub.: 11.81 mg CO_2; 2.53 mg H_2O. 5.07 mg sub.: 12.04 mg CO_2; 2.55 mg H_2O. 6.49 mg sub.: 0.775 ml N_2 (21°, 755 mm). 5.59 mg sub.: 0.671 ml N_2 (21°, 755 mm). Found %: C 64.72, 64.81; H 5.68; 5.63; N 13.82, 13.89. $C_{11}H_{12}O_2N_2$. Calculated %: C 64.70; H 5.88; N 13.72.

The obtained substance is 3-N-methyl-4-phenyldihydrouracil.

3-N-Methyl-4-phenyl-5-ethyldihydrouracil. 0.3 g (0.001 mole) of α-ethyl-β-phenyl-β,N-1-methylureidopropionic acid with a m. p. of 208° and 8 ml of 12% hydrochloric acid were boiled in a flask with a reflux condenser on a grid of 2.5 hours. In the first ten minutes of heating, all of the ureido acid was dissolved. On the completion of the heating, the solution was filtered, cooled; thereupon fine, lustrous crystals were precipitated out. In order to achieve full crystallization, the precipitate was allowed to stand for several hours. The crystals which were isolated were filtered, washed with water, and then several times with ether. The yield was 0.25 g (90%), the m. p. was 137°. After recrystallization from alcohol the substance melted at 137-138°.

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* First prepared by Evans and Johnson [5] but the conditions of conducting of the experiment were not described in detail.

5.13 mg sub.: 12.66 mg CO_2; 3.18 mg H_2O. 4.83 mg sub.: 11.93 mg CO_2; 3.02 mg H_2O. 4.31 mg sub.: 0.463 ml N_2 (22.5°, 747 mm). 5.69 mg sub.: 0.605 ml N_2 (22.5°, 747 mm). Found %: C 67.34, 67.41; H 6.93, 7.00; N 12.20, 12.07. $C_{13}H_{16}O_2N_2$. Calculated %: C 67.24; H 6.89; N 12.06.

The obtained substance was 3-N-methyl-4-phenyl-5-ethyldihydrouracil; it is difficultly soluble in water, ether, and benzene, and is quite soluble in alcohol.

3-N-Methyl-4-phenyl-5-n-butyldihydrouracil. 0.58 g (0.002 mole) of α-n-butyl-β-phenyl-β,N-1-methylureidopropionic acid with a m. p. of 213-214° and 15 ml of 12% hydrochloric acid were heated in a round-bottomed flask with a reflux condenser on a grid for one hour; thereupon, the precipitate was not dissolved; 5 ml more of hydrochloric acid (1 : 1) was added and the mixture was boiled for 3 more hours. On the completion of the heating, the solution was cooled; thereupon, white crystals were isolated. The precipitate was filtered, washed with water, and then several times with anhydrous ether. The yield was 0.52 g, the m. p. was 192-194°. After recrystallization from a mixture of alcohol and anhydrous ether, 0.45 g (83%) of a substance with a m. p. of 195-197° was isolated. A mixed sample of the obtained substance with pure α-n-butyl-β-phenyl-β,N-1-methylureidopropionic acid gave a depression of the melting point (m. p. 183-187°).

After two recrystallizations from alcohol, the substance had a m. p. of 197.5-199°.

5.65 mg sub.: 14.34 mg CO_2; 3.82 mg H_2O. 5.38 mg sub.: 13.68 mg CO_2; 3.58 mg H_2O. 6.77 mg sub.: 0.637 ml N_2 (20.5°, 751 mm). 6.19 mg sub.: 0.576 ml N_2 (20.5°, 751 mm). Found %: C 69.26, 69.39, H 7.56, 7.44; N 10.81, 10.70. $C_{15}H_{20}O_2N_2$. Calculated %: C 69.23; H 7.69; N 10.77.

The obtained compound is 3-N-methyl-4-phenyl-5-n-butyldihydrouracil, which crystallizes from alcohol in the form of fine, colorless needles; it is difficultly soluble in the common organic solvents, and quite soluble in hot alcohol; it is insoluble in water and mineral acids.

SUMMARY

1. The following α-alkyl-β-phenyl-β,N-alkylaminopropionic acids have been synthesized by the addition of alkylmalonic acids to Schiff's base: α-ethyl-β-phenyl-β,N-methylaminopropionic, α-n-butyl-β-phenyl-β,N-methylaminopropionic, and β-phenyl-β,N-benzylaminopropionic acids.

This creates the basis for the confirmation of the correctness of the first scheme of the formation of β-amino acids.

2. It has been established that the alkylated β-amino acids are obtained in two diastereoisomeric forms.*

3. Carboethoxy derivatives of the following acids have been prepared: β-phenyl-β,N-methylaminopropionic, α-ethyl-β-phenyl-β,N-methylaminopropionic, and α-benzyl-β-phenyl-β,N-methylaminopropionic.

4. The following new ureido acids have been isolated: α-ethyl-β-phenyl-β,N-1-methylureidopropionic and α-n-butyl-β-phenyl-β,N-1-methylureidopropionic.

5. The following new alkylated dihydrouracils have been prepared, by means of the closing of the pyrimidine ring, from the corresponding alkylated β-ureido acids: 3-N-methyl-4-phenyl-5-ethyl- and 3-N-methyl-4-phenyl-5-n-butyl-dihydrouracils.

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* All of the below-described derivatives were obtained for only one of the diastereoisomers.

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THE REACTIONS OF TRICHLOROPHOSPHAZOSULFONARYLS WITH PHENOLS AND THE AROMATIC ESTERS OF ARYLSULFONAMIDOPHOSPHORIC ACIDS

A. V. Kirsanov and V. I. Shevchenko

Trichlorophosphazosulfonaryls, like phosphorus oxychloride [1], react with phenols with considerably more difficulty than with alcohols [2]. On the interaction of trichlorophosphazosulfonphenyl with phenol, the evolution of hydrogen chloride just barely begins at 100°, and on the interaction of phenol with α-trichlorophosphazosulfonnaphthyl it does not begin until 140-150°.

The reaction of trichlorophosphazosulfonaryls with sodium phenolate takes place incomparably more easily. The reaction occurs according to the scheme:

$$ArSO_2N=PCl_3 + 3C_6H_5ONa \rightarrow 3NaCl + ArSO_2N=P(OC_6H_5)_3,$$

that is, with the formation of the triphenyl ester of the arylsulfonimidophosphoric acids.

Thus, the following triphenyl esters were prepared:

$$ArSO_2N=P(OC_6H_5)_3, \text{ where: } Ar = C_6H_5,\ o\text{-}CH_3C_6H_4,\ \alpha\text{-}C_{10}H_7 \text{ and } \beta\text{-}C_{10}H_7.$$

The triphenyl esters of the arylsulfonimidophosphoric acids are colorless, odorless and tasteless crystalline substances. Chemically, the full phenyl esters of the arylsulfonimidophosphoric acids are stable, neutral substances. They, like the trialkyl esters [2], are fully stable to the action of water, and do not react with it even on prolonged boiling. They are also stable against the action of dilute aqueous solutions of mineral acids and bases.

The stability of the triphenyl esters of the arylsulfonimidophosphoric acids to the action of dilute aqueous solutions of sodium hydroxide is explained by their insolubility in water. In an aqueous alcohol solution of sodium hydroxide, in which the triphenyl esters are quite soluble, saponification takes place easily and quickly, with the formation of the sodium salts of the diphenyl esters of the arylsulfonamidophosphoric acids, $ArSO_2NNaPO(OC_6H_5)_2$.

Longer heating of the triphenyl esters with a 0.2 N water-alcohol solution of sodium hydroxide does not lead to further saponification; hydrolysis stops with the formation of the sodium salts of the diphenyl esters. In relation to dilute mineral acids, the triphenyl esters of arylsulfonimidophosphoric acids are more stable than they are in relation to bases. However, the stability of the full phenyl esters of the arylsulfonimidophosphoric acids to the action of weak solutions of mineral acids cannot be explained only by their insolubility in water.

The main products of the hydrolysis of the arylsulfonimidophosphoric acids with a 0.2 N water-alcohol solution of hydrochloric acid are the diphenyl esters, which are formed according to the scheme:

$$ArSO_2N=P(OC_6H_5)_3 + H_2O \rightarrow ArSO_2NHPO(OC_6H_5)_2 + C_6H_5OH.$$

The diphenyl esters of our more stable triphenyl esters were also saponified only under more rigid conditions.

The quantitative data on the hydrolysis of the triphenyl esters of arylsulfonimidophosphoric acids through the use of acids, given in the experimental section of this paper, are only approximate, since the quantitative analysis of the mixture of products formed is very difficult to carry out without losses of material. However, for the qualitative characteristics, the obtained data are fully satisfactory.

The diphenyl esters of arylsulfonamidophosphoric acids, like the dialkyl esters [2] are also easily prepared with good yields from the dichloroanhydrides of the arylsulfonamidophosphoric acids and sodium phenolate. The reaction of sodium phenolate with the dichloroanhydrides in the presence of a solvent (benzene) takes place just as easily as with the trichlorophosphazosulfonaryls, according to the scheme:

$$ArSO_2NHPOCl_2 + 3C_6H_5ONa \rightarrow ArSO_2NNaPO(OC_6H_5)_2 + C_6H_5OH + 2NaCl.$$

The sodium salts which have been formed remain in the benzene solution for some time after the completion of the reaction. On the heating of the reaction mixture to boiling, they precipitate out in the solid state. An exception is the sodium salt of the diphenyl ester of phenylsulfonamidophosphoric acid, the benzene solution of which is quite stable. The reaction mixture of Na phenolate with the dichloroanhydride of phenylsulfonamidophosphoric acid in a benzene medium is a homogeneous, clear solution, containing a slimy sodium chloride precipitate on the bottom. However, the dried, crystalline sodium salt of the diphenyl ester of phenylsulfonamidophosphoric acid, is insoluble in benzene.

Attention is attracted to the character of the course of reaction of Na phenolate with the dichloroanhydride of o-tolylsulfonamidophosphoric acid. The reaction mixture, consisting of powdered Na phenolate, finely ground dichloroanhydride, and benzene, on being shaken up, sets at first into a porous, spongy mass; then the mixture begins to warm up (to 50-60°), and the spongy mass goes into solution. Evidently, some intermediate product is first formed, then the reaction takes place according to the scheme given above.

The following diphenyl esters were obtained by the reaction of the dichloroanhydrides of the arylsulfonamidophosphoric acids with sodium phenolate:

$$ArSO_2NHPO(OC_6H_5)_2, \text{ where } Ar = C_6H_5,\ o\text{-}CH_3C_6H_4,\ \alpha\text{-}C_{10}H_7 \text{ and } \beta\text{-}C_{10}H_7.$$

The diphenyl esters of the arylsulfonamidophosphoric acids are colorless, crystalline substances with comparatively high melting points (138-179°).

Chemically, the diphenyl esters are mono-basic acids, which are titrated by one equivalent of a sodium hydroxide solution (with phenolphthalein).

The diphenyl esters of phenylsulfonamidophosphoric acids are very stable in relation to the action of dilute acids and bases.

Under more rigorous conditions (see Experimental section), the diphenyl esters are saponified with the formation of the corresponding sulfamides.

The o-, m-, and p-cresyl esters were prepared in an analogous manner to the preparation of the phenyl esters. Sodium cresolates react with trichlorophosphazosulfonaryls just as easily as sodium phenolates. There is no essential difference in the method of separation of the reaction products, or in the method of carrying out the reaction itself.

The tricresyl esters of phenylsulfonimidophosphoric acid were prepared:

$$C_6H_5SO_2N = P(OAr)_3, \text{ where } Ar = o\text{-},\ m\text{-}, \text{ and } p\text{-}CH_3C_6H_4;$$

those of α-naphthylsulfonimidophosphoric acid:

$$\alpha\text{-}C_{10}H_7SO_2N = P(OAr)_3, \text{ where } Ar = o\text{- and } p\text{-}CH_3C_6H_4$$

and the p-tricresyl ester of o-tolylsulfonimidophosphoric acid:

$$o\text{-}CH_3C_6H_4SO_2N = P(OC_6H_4CH_3\text{-}p)_3.$$

The tricresyl esters, with the exception of the o-tricresyl ester of phenylsulfonimidophosphoric acid, are thick, oily liquids. They did not crystallize either on long standing (over a year), or on cooling in a mixture of snow and salt. The liquid tricresyl esters were not obtained in the chemically pure state, since they could not be distilled without decomposition.

Chemically, the tricresyl esters are similar to the full phenyl esters. They, like the phenyl esters, are not hydrolyzed by water and dilute aqueous solutions of mineral acids and bases. A water-alcohol solution of sodium hydroxide easily saponifies the tricresyl esters, with the formation of the sodium salts of the dicresyl esters.

The m-dicresyl ester of phenylsulfonamidophosphoric acid, $C_6H_5SO_2NHPO(OC_6H_4CH_3\text{-}m)_2$, the p-dicresyl ester of o-tolylsulfonamidophosphoric acid

$$o\text{-}CH_3C_6H_4SO_2NHPO(OC_6H_4CH_3\text{-}p)_2$$

and the o-dicresyl ester of α-naphthylsulfonamidophosphoric acid

$$\alpha\text{-}C_{10}H_7SO_2NHPO(OC_6H_4CH_3\text{-}o)_2$$

and the p-dicresyl ester of α-naphthylsulfonamidophosphoric acid

$$\alpha\text{-}C_{10}H_7SO_2NHPO(OC_6H_4CH_3\text{-}p)_2,$$

were prepared by the hydrolysis of the tricresyl esters with a water-alcohol solution of sodium hydroxide.

The dicresyl esters of phenylsulfonamidophosphoric acids, like the diphenyl esters, are easily prepared with good yields from the dichloroanhydrides of the arylsulfonamidophosphoric acids and sodium cresolates. The dicresyl esters of phenylsulfonamidophosphoric acid:

$$C_6H_5SO_2NHPO(OAr)_2 \text{ where } Ar = o\text{-}, m\text{- and } p\text{-}CH_3C_6H_4$$

and the p-dicresyl esters:

$$ArSO_2NHPO(OC_6H_4CH_3\text{-}p)_2, \text{ where } Ar = CH_3C_6H_4\text{-}o, \alpha\text{-}C_{10}H_7 \text{ and } \beta\text{-}C_{10}H_7$$

were prepared by the reactions of the sodium cresolates with the dichloroanhydrides.

The dicresyl esters of the arylsulfonamidophosphoric acids are crystalline substances, which crystallize in well-formed crystals from carbon tetrachloride or alcohol.

The dicresyl esters are insoluble in water. All of the dicresyl and diphenyl esters have a very bitter taste (compare with dibutyl esters [2]).

Chemically the dicresyl esters are mono-basic acids, which are titrated with one equivalent of a sodium hydroxide solution (to phenolphthalein). Exactly like the diphenyl esters, they are stable against the action of dilute solutions of mineral acids, and bases.

It would be interesting to prepare the full phenyl esters of the arylsulfonamidophosphoric acids, which would contain in the phenyl ring some strong electronegative group, e. g. NO_2.

The nitrophenyl esters of the arylsulfonimidophosphoric acids were prepared by the reaction of the trichlorophosphazosulfonaryls with sodium o-nitrophenolate; these nitrophenyl esters differ sharply in their properties from the corresponding phenyl esters.

The reaction of sodium o-nitrophenolate with the trichlorophosphazosulfonaryls takes place with difficultly, upon long heating, according to the scheme:

$$ArSO_2N = PCl_3 + 3NaOC_6H_4NO_2 \rightarrow 3NaCl + ArSO_2N = P(OC_6H_4NO_2)_3;$$

this is even more true of its reaction with the dichloroanhydrides of the arylsulfonamidophosphoric acids.

The trinitrotriphenyl esters, unlike the triphenyl esters, are very easily hydrolyzed by water; it is therefore necessary to use completely dry solvents during their isolation and purification.

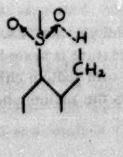
Thus, the o-trinitrotriphenyl esters were prepared

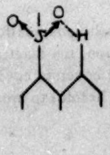
$$ArSO_2N = P(OC_6H_4NO_2\text{-}o)_3, \text{ where } Ar = C_6H_5, o\text{-}CH_3C_6H_4 \text{ and } \alpha\text{-}C_{10}H_7.$$

The trinitrotriphenyl esters are crystalline substances, yellow in color, with the odor of nitrophenol. They are quite soluble in hot benzene, acetone, hot alcohol, and are insoluble in ether and water. They crystallize from benzene as well-formed, clear, yellow prisms.

Our attention is attracted to the high melting points of the full nitrophenyl esters of o-tolyl- and α-naphthyl sulfonimidophosphoric acids (152 and 148°). All of the other full esters, prepared or described in this paper, are either liquids, or crystalline substances which melt at temperatures not higher than 95°.

It is very probable that the comparatively high melting points of the o-tolyl- and α-naphthyl derivatives are explained by the fact that these compounds have identical characteristic structural details; namely, in both of these types of compounds, the o-position in the nucleus in relation to the sulfo group, is substituted, and has the possibility of the formation of a hydrogen bond with the atom of oxygen linked with the sulfur,





Therefore, the full esters of o-tolylsulfonimidophosphoric acids, in comparison with the corresponding esters of phenyl- and p-tolylsulfonimidophosphoric acids, have higher melting points, crystallize better, and are somewhat less soluble. In this relationship, the esters of o-tolylsulfonimidophosphoric acids are more similar to the corresponding derivatives of α-naphthylsulfonimidophosphoric acids than to the phenyl or p-tolyl derivatives.

In their chemical properties (the great ease of hydrolysis), the full nitrophenyl esters are more similar to the mixed anhydrides than to the esters. On dissolution in 96% alcohol, they are immediately hydrolyzed with the formation of nitrophenol and the dinitrophenyl ester of arylsulfonamidophosphoric acid, according to the scheme:

$$ArSO_2N{=}P(OC_6H_4NO_2\text{-}o)_3 + H_2O \rightarrow ArSO_2NHPO(OC_6H_4NO_2\text{-}o)_2 + HOC_6H_4NO_2.$$

In relation to the moisture of the air, for comparatively short periods, the crystals of the full nitrophenol esters are quite stable. However, on long standing in the air, they slowly decompose. Thus, on the storing of pure trinitrotriphenyl esters in flasks that were not tightly covered over a period of a year, small admixtures of regular crystals, which melted at 45° and did not give a depression of the melting point with o-nitrophenol, were detected. It is interesting that the o-nitrophenol which was isolated on long standing was not distributed evenly throughout the entire mass of the trinitrotriphenyl ester, but was concentrated in separate places in the form of well-formed clear crystals, which increased in size as the length of time of storage increased. This is explained, probably, by the great volitility of o-nitrophenol at room temperature.

On heating with water, the full nitrophenyl esters are hydrolyzed more slowly than in alcohol solutions, which is probably explained by their lower solubility in water.

The dinitrodiphenyl esters of the arylsulfonamidophosphoric acids were also prepared by the reaction of sodium o-nitrophenolate with the dichloroanhydrides of the corresponding acids. The dichloroanhydrides of the arylsulfonamidophosphoric acids react with sodium o-nitrophenolate with great difficulty. In order to prepare the dinitrodiphenyl esters of phenyl- and o-tolylsulfonamidophosphoric acids, a mixture consisting of sodium o-nitrophenolate, the dichloroanhydride of the acid, and benzene is heated to boiling for 20 hours. Even with this treatment, the reaction does not take place completely. On the heating of the dichloroanhydride of α-naphthylsulfonamidophosphoric acid with sodium o-nitrophenolate in boiling benzene for 50 hours, only a small part of the original substances enter into the reaction.

The dinitrodiphenyl esters were prepared by the reaction of the dichloroanhydrides with sodium o-nitrophenolate:

$$ArSO_2NHPO(OC_6H_4NO_2\text{-}o)_2, \text{ where } Ar{=}\,C_6H_5 \text{ and } o\text{-}CH_3C_6H_4.$$

It is more convenient to prepare the dinitrodiphenyl ester of α-naphthylsulfonamidophosphoric acid, $\alpha\text{-}C_{10}H_7SO_2NHPO(OC_6H_4NO_2\text{-}o)_2$, from the corresponding full nitrophenyl ester on its dissolution in alcohol.

The dinitrodiphenyl esters of the arylsulfonamidophosphoric acids are colorless crystalline substances, which crystallize well from alcohol.

The dinitrodiphenyl esters are mono-basic acids. They are titrated by one equivalent of sodium hydroxide (with phenolphthalein). They are stable in relation to water, not hydrolyzing to any considerable extent even on long boiling with water, but they are easily hydrolyzed on heating with a normal solution of sodium hydroxide

EXPERIMENTAL

The preparation of the triphenyl esters of arylsulfonimidophosphoric acids. In a flask, with a volume of 150-200 ml, were placed 0.06 mole (7.0 g) of dry, finely ground sodium phenolate, and 10 ml of dry benzene; a solution of 0.02 mole of trichlorophosphazosulfonaryl in 40 ml of benzene was added with constant stirring. In the case of trichlorophosphazosulfonphenyl and o-tolyl, the reaction takes place easily on the warning of the reaction mixture to 50-60°. The sodium phenolate quickly disappears and a slimy sodium chloride precipitate is formed. For the completion of the reaction, the flask is fastened to a reflux condenser and the mixture is heated over a boiling water bath for 30 minutes.

In the case of α- and β-trichlorophosphazosulfonaphthyls, the reaction takes place slowly with a small amount of heat. In order to carry out the reaction, the reaction mixture is heated to boiling for 1 hour. The sodium phenolate is sometimes whipped into a clot which becomes covered with sodium chloride; this slows down the reaction a great deal, or causes it to stop entirely. It is helpful to break up the sodium phenolate clot which has been formed, with a glass rod.

After the completion of the reaction, the sodium chloride is drawn off, and the filtrate is evaporated in a vacuum over a boiling water bath until all of the solvent has been driven off. The residue, which is damp triphenyl ester, is either crystallized immediately, or is first worked with a 0.05 N solution of sodium hydroxide. In the latter case, the pure products are ordinarily obtained after only one crystallization.

The triphenyl esters are easily dissolved in dioxane, acetone, chloroform, benzene, hot alcohol, and hot carbon tetrachloride, and dissolved with more difficulty in ether.

For the triphenyl ester of phenylsulfonimidophosphoric acid, the yield was 8.50 g (91.4%). It is difficultly soluble in petroleum ether. It crystallizes well from alcohol, carbon tetrachloride, and petroleum ether. The prisms (from alcohol) have a melting point of 85-86°.

Found %: N 2.98, 2.90. $C_{24}H_{20}O_5NSP$. Calculated %: N 3.01.

For the triphenyl ester of o-tolylsulfonimidophosphoric acid the yield was 7.52 g (78.5%).

The small prism (from alcohol) had a melting point of 79-80°.

Found %: N 3.03, 2.96. $C_{25}H_{22}O_5NSP$. Calculated %: N 2.92.

For the triphenyl ester of β-naphthylsulfonimidophosphoric acid the yield was 7.93 g (77.0%). They were difficultly soluble in petroleum ether, and insoluble in water. The prisms (from carbon tetrachloride or alcohol) had a melting point of 94-95°.

Found %: N 2.74, 2.84. $C_{28}H_{22}O_5NSP$. Calculated %: N 2.72.

For the triphenyl ester of β-naphthylsulfonimidophosphoric acid the yield was 8.61 g (83.6%). It was insoluble in water and petroleum ether. The melting point of the small prisms (from alcohol or carbon tetrachloride) was 90-91°.

Found %: N 2.70, 2.81. $C_{28}H_{22}O_5NSP$. Calculated %: N 2.72.

The hydrolysis of the triphenyl esters of the arylsulfonimidophosphoric acids with alcohol solutions of sodium hydroxide. In a small flask, with a volume of 50 ml, equipped with a reflux condenser, were placed 0.001 mole of the full phenyl ester of the arylsulfonimidophosphoric acid, and 5 ml of a 1.0 N solution of sodium hydroxide and 20 ml of alcohol were added. The mixture was heated over a boiling water bath for 1 hour, after which the alcohol was distilled off in a vacuum. The residue, after the alcohol was driven off, dissolved completely in water, and thus did not contain triphenyl ester. After the acidification of the solution with hydrochloric or sulfuric acid until it gave an acid reaction with a Congo red indicator, the diphenyl esters were precipitated in the form of thick oil, which was easily crystallized on being stirred slightly with a glass rod. The precipitate was filtered with suction, washed well with water and dried. The diphenyl ethers obtained in this way have a clear melting point. A mixed sample with diphenyl esters obtained from the dichloranhydrides of the arylsulfonamidophosphoric acids and sodium phenolate, did not give a depression of the melting point. The yield of the diphenyl esters of the arylsulfonamidophosphoric acids obtained by alkaline hydrolysis, varied between 90.9 and 96.5%;

The hydrolysis of the triphenyl esters of arylsulfonimidophosphoric acids by an alcohol solution of hydrochloric acid. 0.01 g-mole of the triphenyl ester of arylsulfonimidophosphoric acid was placed in a 500 ml flask equipped with a reflux condenser; 200 ml of alcohol and 50 ml of a 1.0 N aqueous solution of hydrochloric acid was added. The mixture was heated to boiling for one hour. After the distilling off of the alcohol in a vacuum, a heavy oily layer was formed which was not soluble in water. The acidified, aqueous solution was decanted and discarded and the oily layer was washed with water. Ten ml of a 1.0 N solution of sodium hydroxide was added to the oily residue. They were well washed and the oil which was not dissolved was washed with water. After the first washing, the oily liquid ordinarily begins to crystallize. The crystalline precipitate which consists of that part of the triphenyl ester which has not reacted, and a small quantity of admixtures, is dried and crystallized. The yield is from 56.1% to 62.5%. The alkaline solution and the wash water are mixed and filtered. After acidification with hydrochloric acid until the solution gives an acid reaction to a Congo red indicator, a crystalline precipitate is formed; this precipitate is the diphenyl ester. The diphenyl ester is separated, washed, and dried. Its melting point differs by 1-2° from that of the pure substance. The yield is from 16.6% to 18.0%.

The preparation of the diphenyl esters of arylsulfonamidophosphoric acids. 50 ml of benzene was added with stirring to a mixture consisting of 0.02 mole of the dichloroanhydride of an arylsulfonamidophosphoric acid, finely ground, and 0.06 -mole of sodium phenolate. The reaction takes place gently with little evolution of heat. The sodium salts of the diphenyl esters, formed as a result of the reaction, remain in solution, but on the heating of the reaction mixture to boiling, they are precipitated in the crystalline state. The reaction mixture is evaporated until dry, the solvent is distilled off in a vacuum over a boiling water bath. 200 ml of water is added to the residue and the mixture is agitated until the residue dissolves. (The sodium salt of the diphenyl ester of α-naphthylsulfonamidophosphoric acid is difficultly soluble in cold water. For solution, it is necessary to gently heat the mixture. In hot water the salt is dissolved very easily.) The solutions of the sodium salts are acidified with a 2.0 N solution of sulfuric or hydrochloric acid until they give an acid reaction with a Congo red indicator. The diphenyl esters are difficultly soluble in water and precipitate from an acidified solution in the form of a thick, viscous mass which is easily and completely crystallized. The diphenyl esters which have been crystallized are filtered with suction, washed with water, dried, and crystallized. The diphenyl ester of phenylsulfonamidophosphoric acid gave a yield of 7.02 g (90.2%). The ester is quite soluble in acetone, chloroform, hot alcohol, and difficultly soluble in hot carbon tetrachloride and hot ether. The diphenyl ester is not soluble in water and petroleum ether. It crystallizes very well from benzene and alcohol in the form of transparent, colorless crystals. From carbon tetrachloride it precipitates in the form of long needles with a melting point of 145-146°.

Found %: N 3.49, 3.52. Equivalent (according to phenolphthalein) 0.999, 0.995. $C_{18}H_{16}O_5NSP$. Calculated %: N 3.60. Equivalent 1.00.

For the diphenyl ester of o-tolylsulfonamidophosphoric acid, the yield was 6.65 g (82.5%). It is easily soluble in acetone, chloroform, hot alcohol and benzene, and difficultly soluble in ether; it is insoluble in water. It crystallizes well from alcohol in the form of fine prisms with a melting point of 160-161°.

Found %: N 3.56. Equivalent (according to phenolphthalein) 0.996, 0.997. $C_{19}H_{18}O_5NSP$. Calculated %: N 3.47. Equivalent. 1.00.

The diphenyl ester of α-naphthylsulfonamidophosphoric acid – yield, 7.00 g (79.7%). From dilute alcohol (50%), well formed fine prisms were precipitated with an m. p. of 137-138°. The ester is easily dissolved in acetone, chloroform, dioxane, and alcohol; it is difficultly soluble in hot water.

Found %: N 3.30. Equivalent 1.004, 0.988. $C_{22}H_{18}O_5NSP$. Calculated %: N 3.19. Equivalent 1.00.

The diphenyl ester of β-naphthylsulfonamidophosphoric acid – yield 7.14 g (81.3%). This substance is comparatively quite soluble in hot acetone, chloroform, and benzene and precipitates from these solvents in the form of very fine transparent prisms; it is insoluble in water, ether, petroleum ether and carbon tetrachloride. It crystallizes well from alcohol; m. p. equals 178-179°.

Found %: N 3.27, 3.25. Equivalent (according to phenolphthalein) 0.947, 0.978. $C_{22}H_{18}O_5NSP$. Calculated %: 3.19, Equivalent 1.00.

The hydrolysis of the diphenyl esters of phenyl- and α-naphthylsulfonamidophosphoric acids. 0.003 mole of the diphenyl ester was boiled with 30 ml of a 1 N water-alcohol solution of hydrochloric acid (15 ml of a 2.0 N aqueous solution of hydrochloric acid and 15 ml of alcohol) for 24 hours. After the distilling off of the alcohol in a vacuum over a water bath, an oil was precipitated; the oil quickly began to crystallize. In order to separate the arylsulfamide from the diphenyl ester, the reaction product was washed with water, transferred to a flask and neutralized with a 0.2 N solution of sodium hydroxide until it gave an alkaline reaction to phenolphthalein. Then the mixture was heated znd filtered with suction in the hot state. The arylsulfamide remained on the filter: the sodium salt of the diphenyl ester was found in the filtrate. After the cooling of the solution, the sodium salt of the diphenyl ester of α-naphthyl-sulfomanidophosphoric acid was precipitated in the form of very small, lustrous plates.

The arylsulfamides which were separated were identified by the melting point of a mixed sample with the pure amide.

0.16 g (34.0%) of the phenylsulfamide was isolated, m. p. 148-150°; 0.3 g (48.3%) of the α-naphthylsulfamide was separated, m. p. 150-153°.

The preparation of the tricresyl esters of the arylsulfonimidophosphoric acids. In a 100 ml flask was placed 0.03 mole (3.9 g) of dry, finely pulverized o- m- or p-sodium cresolate, and a solution of 0.01 mole of trichlorophosphazosulfonaryl in 20 ml of benzene was added with stirring. The reaction took place energetically with the heating of the mixture, sometimes up to the boiling point of the solvent. The sodium cresolate quickly disappeared and a slimy precipitate of sodium chloride was formed. The reaction mixture was allowed to cool to room temperature and then 30 ml of benzene and 100 ml of a 0.05 N solution of sodium hydroxide was added, after which the mixture was shaken up in a separatory funnel. The benzene extract was washed twice with 100 ml of water containing sodium chloride, filtered and dried with sodium sulfate. The dry benzene extract, after filtering, was evaporated, and the solvent was driven off in the vacuum of a water-jet pump, over a boiling water bath. In the flask was left the tricresyl ester in the form of a thick oily liquid which had a slight yellow color. In the case of the o-tricresyl ester of phenylsulfonimidophosphoric acid, the oily liquid which was obtained was easily crystallized. The tricresyl esters are quite soluble in acetone, benzene, alcohol and chloroform.

For the o-tricresyl ester of phenylsulfonimidophosphoric acid, the yield was 4.36 g (84.0%). Transparent, colorless needles were obtained (from alcohol); m. p. 90-91°.

Found %: N 2.77. $C_{27}H_{20}O_5NSP$. Calculated %: N 2.76.

The m-tricresyl ester of phenylsulfonimidophosphoric acid gave a yield of 3.7 g (72.9%). The thick transparent liquid, yellow in color, is insoluble in water and petroleum ether.

Found %: N 2.85, 2.80. $C_{27}H_{26}O_5NSP$. Calculated %: N 2.76.

The p-tricresyl ester of phenylsulfonimidophosphoric acid gave a yield of 4.37 g (86.1%). It is a thick, colorless, yellow liquid which is not crystallized on cooling in a freezing mixture.

Found %: N 2.81, 2.77. $C_{27}H_{26}O_5NSP$. Calculated %: N 2.76.

The p-tricresyl ester of o-tolylsulfonimidophosphoric acid gave a yield of 3.2 g (63.1%). The thick, clear, yellow liquid is insoluble in water and petroleum ether. It was not analyzed. It was identified by conversion into the corresponding dicresyl ester (see below).

For the o-tricresyl ester of α-naphthylsulfonimidophosphoric acid, a yield of 3.62 g (65.0%) was obtained. The ester is a very viscous, thick liquid that is yellow in color. It was not analyzed. It was identified by conversion into the corresponding dicresyl ester (see below).

For the p-tricresyl ester of α-naphthylsulfonimidophosphoric acid, the yield was 4.02 g (72.2%). The thick, oily liquid is yellow in color. It was not analyzed. It was identified by conversion into the corresponding dicresyl ester (see below).

The saponification of the tricresyl esters with a water-alcohol solution of sodium hydroxide. 0.002 mole of the full tricresyl ester of the arylsulfonimidophosphoric acid was poured into a 50 ml flask, connected to a reflux condenser; 20 ml of alcohol and 5 ml of a 1.0 N solution of sodium hydroxide was then added. The mixture was heated to boiling for 1 hour, after which the alcohol was distilled off in a vacuum. The precipitate, after the alcohol was driven off, was wholly soluble in water, and therefore, did not contain the tricresyl ester. After the acidification of the aqueous solution with hydrochloric acid (6 ml of a 2.0 N solution), the dicresyl ester was precipitated; it crystallized slowly on being rubbed slightly with a glass rod. The dicresyl ester which is precipitated in the form of an oily layer, is crystallized with considerably more ease if the acidified aqueous solution is decanted with the precipitated oil, and it is well washed with water. The crystalline precipitate is separated, washed, and recrystallized.

By this method were obtained:

The m-dicresyl ester of o-tolylsulfonamidophosphoric acid, with a yield of 0.52 g (62.4%). It is quite soluble in acetone, chloroform, ether, benzene, hot carbon tetrachloride, and hot alcohol. Well-formed prisms are obtained on crystallization from carbon tetrachloride or dilute alcohol (70%); their m. p. is 107-109°. A mixed sample with the m-dicresyl ester, obtained from m-sodium cresylate and the dichloroanhydride of phenylsulfonamidophosphoric acid, did not give a depression of the melting point.

Found: Equivalent (according to phenolphthalein) 0.97. $C_{20}H_{20}O_5NSP$. Calculated: Equivalent 1.00.

The p-dicresyl ester of o-tolylsulfonamidophosphoric acid, with a yield of 0.68 g (78.8%). The ester is quite soluble in acetone, dioxane, benzene, ether, hot carbon tetrachloride and alcohol. It crystallizes well from carbon tetrachloride and dilute alcohol (70%) in the form of fine, colorless, clear prisms, with a m. p. of 116-117°.

The mixed sample with the p-dicresyl ester, prepared from p-sodium cresylate and the dichloroanhydride of o-tolylsulfonamidophosphoric acid, did not give a depression of the melting point.

Found: Equivalent (according to phenolphthalein) 1.015, 1.016. $C_{21}H_{22}O_5NSP$. Calculated: Equivalent 1.00.

The o-dicresyl ester of α-naphthylsulfonamidophosphoric acid with a yield of 0.76 g (81.3%). The o-dicresyl ester, which is precipitated on the acidification of the alkaline hydrolysis, has the form of a clear, sticky tar, which crystallizes very slowly. On crystallization from alcohol, fine needles with a melting point of 134-136° are obtained.

The ester is quite soluble in acetone, dioxane, ether, and benzene, and is insoluble in carbon tetrachloride and water. It crystallizes well from benzene and alcohol.

Found: Equivalent (according to phenolphthalein) 0.994. $C_{24}H_{22}O_5NSP$. Calculated: Equivalent 1.00.

The yield of p-dicresyl ester of α-naphthylsulfonamidophosphoric acid was 0.78 g (83.4%). After crystallization from alcohol. long needles came down, m.p. 168-169°. A mixed sample with the dicresyl ester prepared from sodium p-cresylate and the dichloroanhydride of α-naphthylsulfonamidophosphoric acid did not give a melting point depression. The ester readily dissolved in acetone, hot benzene, and hot alcohol, and did not dissolve in carbon tetrachloride, ether, or water.

Found: Equivalent (according to phenolphthalein) 1.03. $C_{24}H_{22}O_5NSP$. Calculated: Equivalent 1.00.

The preparation of the dicresyl esters from sodium cresylate and the dichloroanhydrides of the arylsulfonamidophosphoric acids. 20.0 ml of benzene was added with stirring to a mixture of 0.01 mole of finely pulverized dichloroanhydride of the arylsulfonamidophosphoric acid, and 0.03 mole (3.9 g) of sodium cresylate. The reaction took place gently, with little generation of heat (60-70°). The sodium chloride was filtered with suction and the filtrate was evaporated, the solvent being distilled off in a vacuum over a boiling water bath. The residue was dissolved in 100 ml of hot water and the solution was acidified with hydrochloric acid until it gave an acid reaction with a Congo red indicator. The acidified aqueous solution was decanted with the oily precipitate, which was washed with water and allowed to stand until the following day for crystallization. After the dicresyl ester has begun to crystallize, it is washed with water, separated, and dried. For purification it is crystallized from alcohol.

In this way were obtained:

The o-dicresyl ester of phenylsulfonamidophosphoric acid with a yield of 3.51 g (84.0%). The ester is quite soluble in acetone, benzene, hot carbon tetrachloride, and boiling alcohol; the dicresyl ester is insoluble in water and petroleum ether. It crystallizes well from carbon tetrachloride and alcohol (small, fine prisms) the melting point of the crystals being 136-137°.

Found: Equivalent (according to phenolphthalein) 1.023, 1.013. $C_{20}H_{20}O_5NSP$. Calculated: Equivalent 1.00.

The m-dicresyl ester of phenylsulfonamidophosphoric acid, with a yield of 2.95 g (70.6%). After crystallization from alcohol, the crystals melt at 107-109°. The substance is titrated with phenolphthalein as a monobasic acid. A mixed sample with the dicresyl ester obtained by the saponification of the full ester, did not give a lowering of the melting point.

The p-dicresyl ester of phenylsulfonamidophosphoric acid, with a yield of 3.71 g (88.9%). Quite coarse, well-formed, colorless crystals are precipitated from alcohol; their m. p. is 172-173°. Unlike the o- -and m-dicresyl esters, the p-dicresyl ester is insoluble in ether and carbon tetrachloride, difficultly soluble in boiling benzene, and is quite soluble in acetone and hot alcohol.

Found: Equivalent (according to phenolphthalein) 0.979, 1.016. $C_{20}H_{20}P_5NSP$. Calculated: Equivalent 1.00.

The p-dicresyl ester of o-tolylsulfonamidophosphoric acid, with a yield of 3.32 g (76.9%). The ester is quite soluble in acetone, benzene, hot carbon tetrachloride, and boiling alcohol, and is insoluble in cold water. It crystallizes well from dilute alcohol (70%) in the form of joined prisms with a m. p. of 116-117°.

Found: Equivalent (according to phenolphthalein) 0.965. $C_{21}H_{22}O_5NSP$. Calculated: Equivalent 1.00.

The p-dicresyl ester of α-naphthylsulfonamidophosphoric acid, with a yield of 3.0 g (64.2%), m. p. 168-169°. The substance was titrated with phenolphthalein as a monobasic acid. A mixed sample with the dicresyl ester, prepared by the saponification of the full ester, did not give a depression of the melting point.

The p-dicresyl ester of β-naphthylsulfonamidophosphoric acid with a yield of 3.81 g (81.5%). It is quite soluble in acetone, hot alcohol and boiling benzene; it is insoluble in ether, water and carbon tetrachloride. It crystallizes well from benzene and alcohol, in the form of fine, small prisms with a melting point of 161-162°

Found: Equivalent (according to phenolphthalein) 0.955, 0.966. $C_{24}H_{22}O_5NSP$. Calculated: Equivalent 1.00.

The preparation of the o-trinitrotriphenyl esters of the arylsulfonimidophosphoric acids. In a round-bottomed flask with a volume of 100 ml connected with a reflux condenser, was placed 0.02 mole of the trichlorophosphazosulfonaryl, 0.06 mole of the finely ground o-sodium nitrophenolate; 30 ml of dry benzene was added. The mixture was heated for 4 hours on a boiling water bath with constant agitation. After 4 hours of heating there remained a little of the o-nitrophenolate which had not reacted; this did not disappear even on long heating. In the obtaining of the trinitrophenyl ester of the o-naphthylsulfonimidophosphoric acid, the reaction mixture must be heated for not less than 12 hours, since trichlorophosphazosulfonaphthyl reacts with o-sodium nitrophenolate with considerably more difficultl than the trichlorophosphazosulfonphenyl or the o-tolyl. For the separation of the full nitrophenyl esters, 100 ml of benzene was added to the reaction mixture which was then heated and filtered with suction. In the case of α-trichlorophosphazosulfonnaphthyl, it is necessary to use not less than 200 ml of benzene. The benzene extract was then evaporated in a vacuum over a water bath. As the benzene was distilled off, crystals, or more often oily substances which were easily crystallized, were precipitated. The crystalline residue was washed with a small quantity of ether and crystallized from benzene.

In this way we obtained:

The o-trinitrotriphenyl ester of phenylsulfonimidophosphoric acid, with a yield of 9.46 g (78.8%). More than 65 g of the ester was dissolved in 100 ml of boiling benzene. It is insoluble in water, and ether, and is soluble in acetone. On dissolution in alcohol (rectification), it is quickly hydrolyzed. It precipitates from benzene in the form of yellow prisms with a melting point of 94-95°.

Found %: N 9.27, 9.29. $C_{24}H_{17}O_{12}N_4SP$. Calculated %: N 9.33.

The o-trinitrotriphenyl ester of o-tolysulfonimidophosphoric acid with a yield of 9.1 g (74%). More than 13 g and less than 16 g of the ester dissolve in 100 ml of boiling benzene. It is insoluble in water, ether, carbon tetrachloride, and is difficultly soluble in alcohol, and quite soluble in acetone. It precipitates from benzene in the form of coarse, well-formed yellow prisms with a melting point of 151-152°.

Found %: N 8.86, 8.94. $C_{25}H_{19}O_{11}N_4SP$. Calculated %: N 9.11.

The o-trinitrotriphenyl ester of α-naphthylsulfonimidophosphoric acid, with a yield of 6.8 g (52.3%). More than 14 g and less than 20 g was dissolved in 100 ml of boiling benzene. From benzene it is precipitated in the form of fine, clear, yellow prisms with a m. p. of 147-148°. The ester is insoluble in water, ethyl ether, petroleum ether, carbon tetrachloride, and is difficultly soluble in alcohol.

Found %: N 8.41, 8.37. $C_{28}H_{19}O_{11}N_4SP$. Calculated %: N 8.61.

The hydrolysis of the full nitrophenyl esters of the arylsulfonimidophosphoric acids. The preparation of the o-dinitrodiphenyl ester of phenylsulfonamidophosphoric acid. 6.0 g (0.01 mole) of the full o-nitrophenyl ester of phenylsulfonimidophosphoric acid was dissolved in 10 ml of boiling alcohol (rectification) and was allowed to crystallize. Upon a quick crystallization, fine, colorless crystals were precipitated; m. p. equals 150-151°, yield 3.85 g (80.4%). Repeated crystallization from alcohol gave a completely pure substance with a clear m. p. of 150.5-151.0°. Crystallization from benzene did not raise the melting point. The dinitrodiphenyl ester of phenylsulfonamidophosphoric acid is quite soluble in acetone, hot alcohol, and comparatively soluble in hot water; it is insoluble in petroleum ether and carbon tetrachloride, and difficultly soluble in ether and hot benzene.

Found: Equivalent (according to phenolphthalein) 1.03, 1.00. $C_{18}H_{14}O_7N_3SP$. Calculated: Equivalent. 1.00.

The preparation of the o-dinitrodiphenyl esters of o-tolyl- and α-naphthylsulfonamidophosphoric acids. 0.003 mole of the full nitrophenyl ester was dissolved in 10 ml of boiling alcohol. The alcohol was distilled off in a porcelain dish over a water bath. The residue, which was a thick yellow oil, was easily crystallized on the introduction of several drops of water and gentle rubbing with a glass rod. The product was washed several times with ether, in order to wash off the o-nitrophenyl. After washing with ether, the dinitrodiphenyl ester remained in the form of a white powder; it was crystallized from water or dilute alcohol for purification. It is preferable to crystallize larger quantities of the ester from alcohol.

In this way were obtained:

The o-dinitrodiphenyl ester of o-tolylsulfonamidophosphoric acid with a yield of 0.98 g (66.2%). The ester is quite soluble in acetone and hot alcohol and is comparatively soluble in hot water and difficultly soluble in ether and hot benzene. From concentrated aqueous solutions it falls in the form of agregates of small needles, which originate in the one point. From dilute aqueous solutions, clear, well-formed prisms precipitate; their melting point is 161-162°.

Found %: N 7.95. Equivalent (according to phenolphthalein) 0.990, 1.003, $C_{19}H_{16}O_9N_3SP$. Calculated %: N 7.94. Equivalent 1.00.

The o-dinitrodiphenyl ester of α-naphthylsulfonamidophosphoric acid with a yield of 0.95 g (59.9%). It is comparatively easily soluble in hot water and is crystallized from it in the form of well-formed, clear, fine prisms with a m. p. of 172-173°. The ester is quite soluble in hot water and acetone and is insoluble in benzene, carbon tetrachloride, petroleum ether, and is difficultly soluble in ether.

Found: Equivalent (according to phenolphthalein) 1.01, 1.027. $C_{22}H_{16}O_9N_3SP$. Calculated: Equivalent 1.00.

The reactions of the dichloroanhydrides of the arylsulfonamidophosphoric acids with o-sodium nitrophenolates. In a 200 ml flask connected to a reflux condenser was placed 0.02 mole of the dichloroanhydride of the arylsulfonamidophosphoric acid and 0.06 mole of finely ground o-sodium nitrophenolate; 100 ml of benzene was added. The mixture was heated on the boiling water bath until the main part of the sodium nitrophenolate had reacted; this took about 20 hours. For the separation of the dinitrodiphenyl esters, the reaction mixture was evaporated, the benzene being distilled off in vacuum over a water bath. 200 ml of water was added to the residue, well mixed, and allowed to stand. The aqueous solution was decanted with the oily layer of the nitrophenol and acidified with hydrochloric acid until it gave an acid reaction with Congo red. The dinitrodiphenyl ester was precipitated from the acidified solution in the form of yellow, oily layer, which gradually crystallized. The crystalline precipitate was well washed with water and filtered with suction.

In this way were obtained:

The o-dinitrodiphenyl ester of phenylsulfonamidophosphoric acid, with a yield of 8.43 g (70.3%). After crystallization from alcohol or from water, the melting point was 150-151°. A mixed sample with the dinitrodiphenyl ester, prepared by the hydrolysis of the full nitrophenyl ester, did not give a depression of the melting point.

Found: Equivalent (according to phenolphthalein) 1.005. $C_{18}H_{14}O_9N_3SP$. Calculated: Equivalent 1.00.

The o-Dinitrodiphenyl ester of o-tolylsulfonamidophosphoric acid, with a yield of 3.40 g (34.5%). After crystallization from water, the melting point was 161-162°. A mixed sample with the dinitrodiphenyl ester, prepared by the hydrolysis of the full nitrophenyl ester, melted at the same temperature. The substance was titrated with phenolphthalein as a monobasic acid.

SUMMARY

1. The reactions of the trichlorophosphazosulfonaryls with sodium phenolate, sodium cresylates, and with o-nitrophenolate have been studied.

2. The full aromatic esters of the arylsulfonimidophosphoric acids have been prepared, and their properties have been described.

3. The hydrolysis of the full aromatic esters of the arylsulfonimidophosphoric acids has been studied.

4. The diaryl esters of the arylsulfonamidophosphoric acids have been prepared and their properties have been described.

5. We have prepared and described the o-trinitrotriphenyl esters of the arylsulfonimidophosphoric acids and the o-dinitrodiphenyl esters of the arylsulfonamidophosphoric acids, and have described their properties.

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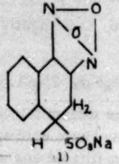
* T. p. = C. B. Translation pagination.

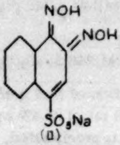
STUDIES IN THE NAPHTHOFUROXANE SERIES

III. 1,2-NAPHTHOQUINONEDIOXIME-4-SULFONIC ACID

S. V. Bogdanov and I. N. Koroleva

As has already been pointed out [1], the bisulfite compounds of naphthofuroxane (I) on the action of soda, (depending on the conditions) are converted into 2-nitro-1-naphthylamine-4-sulfonic acid, or into 2-nitro-1-naphthol-4-sulfonic acid; the following products are also obtained in small quantities: naphthofuroxane, naphthofurazan, and a sulfonic acid of unknown structure. The process takes place differently when the soda is replaced by sodium hydroxide. In this case, when the reaction is carried out at first with cooling, and then at ordinary temperature, with the use of 5 moles of the alkali to one mole of the bisulfite compound, the main product (with yields up to 75%) is 1,2-naphthoquinonedioxime-4-sulfonic acid (II). In addition, 1,2-naphtho-(3',4')-furazan-4-sulfonic acid (III) is obtained, and small quantities of naphthofuroxane and naphthofurazan. On the heating of the bisulfite compounds with a solution of sodium hydroxide, naphthofurazan-4-sulfonic acid is formed, and, in considerably smaller quantities, 2-nitro-1-naphthol-4-sulfonic acid. The above-mentioned sulfonic acid, which was obtained as a by-product in a soda solution, also turned out to be naphthofurazan-4-sulfonic acid. Naphthofurazan-4-sulfonic acid is a product of the further conversion of 1,2-naphthoquinonedioxime-4-sulfonic acid, and is easily obtained on the treatment of the latter with sodium hydroxide or with acetic anhydride. Earlier [2] it was separated from the products of the reaction of 1-nitroso-2-naphthol-4-sulfonic acid with hydroxylamine in an alkaline solution. The formation of naphthofurazan-4-sulfonic acid in a soda solution and 2-nitro-1-naphthol-4-sulfonic acid in a sodium hydroxide solution shows that in both cases the decomposition of the furoxane ring goes in two directions. One of these leads to 2-nitro-1-naphthylamine-4-sulfonic acid, and the other to 1,2-naphthoquinonedioxime-4-sulfonic acid. The degree of basicity of the solution determines only the main path of the reaction.


(I)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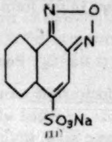
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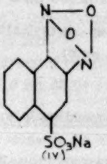
(IV)

1,2-Naphthoquinonedioxime-4-sulfonic acid, on the action of weak hydrochloric acid, is converted into 2-nitro-1-naphthol-4-sulfonic acid, and on reduction with stannous chloride, is converted into 1,2-naphthalenediamine-4-sulfonic acid; on oxidation with nitric acid it converts into naphthofuroxane-4-sulfonic acid (IV).

Naphthofuroxane-4-sulfonic acid, on reduction with zinc (preferably in the presence of a small amount of stannous chloride) is converted into 1,2-naphthalenediamine-4-sulfonic acid, and on the action of potassium hypochlorite and hydrochloric acid it is converted into 4-chloronaphthofuroxane.

EXPERIMENTAL

1,2-Naphthoquinonedioxime-4-sulfonic acid. 28.6 ml (0.5 mole) of 46% sodium hydroxide was added to a suspension of 34.4 g (0.1 mole) of the sodium salt of the bisulfite compound of naphthofuroxane in 175 ml of water, the suspension being first cooled to 5°. The mixture was kept at 5° for two hours, and then at 18-20° for 18 hours. The turbid red-orange solution was filtered, and the residue was washed with water (residue "a"; 0.4 g). 45 ml of 35.4% hydrochloric acid, diluted with 100 ml of water, was gradually added to the filtrate at a temperature of 5-10°. Upon acidification, the evolution of sulfur dioxide gas was detected The suspension of the sodium salt of naphthoquinonedioxime-sulfonic acid which was formed was cooled at 0°, the residue was filtered and washed with water and methyl alcohol; the yield was 24.87-25.8 g, i.e., 72.3-75.0%.

The filtrate, after the addition of sodium acetate, was concentrated by evaporation to a small volume, and the residue which was precipitated was filtered (residue "b").

On the shortening of the length of the experiment to 3 hours and 0.5 hours, the yield fell to 62.5 and 55.7% respectively, and on decreasing the quantity of sodium hydroxide to 2 moles and 1 mole per mole of the bisulfite compound (with the original length of time of the experiment) the yield fell to 51.2 and 46.8%.

On the crystallization of residue ("a") from alcohol naphthofuroxane (m. p. equals 124-125.5°) and naphthofurazan (m. p. 76-78°) were obtained.

On the recrystallization of residue ("b") from water a substance with the properties of naphthofurazan-4-sulfonic acid was obtained (see below). The sulfochloride has a m. p. of 112.5-113.5°.

The sodium salt of naphthoquinonedioximesulfonic acid is quite soluble in water, and more difficultly soluble in alcohol; it is very easily soluble in alkalis, forming an orange solution. Aqueous solutions are colored by iron vitriol to a deep, turbid violet color. In the presence of admixtures of 2-nitroso-1-naphthol-4-sulfonic acid (which is obtained with uncareful separation of the reaction product with hydrochloric acid) a green coloration appears in the first moment after the addition of the iron vitriol; this quickly changes to violet. It crystallizes in the form of long yellow prisms (from water). It contains 3 molecules of water of crystallization, which is not driven off at 100-110°; the substance decomposes at 120-130°.

6.900 mg sub.: 8.800 mg CO_2; 2.380 mg H_2O. 3.916 mg sub.: 0.284 ml N_2 (24°, 732 mm). 0.1050 g sub.: 0.0214 g Na_2SO_4. Found %: C 34.80; H 3.86; N 8.03; Na 6.60. $C_{10}H_7O_5N_2SNa \cdot 3H_2O$. Calculated %: C 34.87; H 3.80; N 8.14; Na 6.68.

The potassium salt is somewhat less soluble in water than the sodium salt. It crystallizes in the form of orange-yellow prisms. It has 1 molecule of water of crystallization, and responds to heating in the same way as the sodium salt.

5.248 mg sub.: 7.204 mg CO_2; 1.234 mg H_2O. 3.697 mg sub.: 0.279 ml N_2 (21°, 745 mm). 0.2203 g sub.: 0.1611 g $BaSO_4$; 0.2362 g sub.: 0.0630 g K_2SO_4. Found %: C 37.44; H 2.63; N 8.59; S 10.04; K 11.97. $C_{10}H_7O_5N_2SK \cdot H_2O$. Calculated %: C 37.03; H 2.80; N 8.64; S 9.89; K 12.06.

The silver salt crystallizes in the form of curved, yellow needles. It is slightly soluble in cold water and decomposes in hot water.

0.4386 g sub.: 11.49 ml 0.1 N NH_4CNS. Found %: Ag 28.26. $C_{10}H_7O_5N_2SAg$. Calculated %: Ag 28.77.

The benzidine salt crystallizes in the form of yellow cubic prisms. It is slightly soluble in water and is decomposed in hot water.

1.8468 g sub.: 49.35 ml 0.1 N $NaNO_2$. Found: M 748.5. $C_{32}H_{28}O_{10}N_6S_2 \cdot 2H_2O$. Calculated: M 756.7.

2-Nitroso-1-naphthol-4-sulfonic acid. A solution of 34.4 g of the sodium salt of naphthoquinonedioximesulfonic acid in 300 ml of water was acidified with 9 ml of 35.4% hydrochloric acid and boiled for 2 hours. The sodium salt of nitrosonaphtholsulfonic acid, which was precipitated, was filtered and washed with water; the yield was 23.0 g (75%). It crystallizes in the form of yellow needles from water. This substance gives an intense green color with iron vitriol. On heating with zinc in the presence of traces of acetic acid, a colorless solution which quickly changes to a blue coloration is formed; on acidification the color becomes red, and on alkalization it becomes green. On reduction with stannous chloride 2-amino-1-naphthol-4-sulfonic acid is formed, and on oxidation with nitric acid 2,4-dinitro-1-naphthol is formed; m. p. 138.5 (decomposes).

1.1162 g sub.: loss on desiccation (120°) 0.1100 g. 0.2788 grams of the dry substance : 0.0704 g Na_2SO_4. Found %: H_2O 9.86; Na 8.18. $C_{10}H_6O_5NSNa \cdot 1.75\ H_2O$. Calculated %: H_2O 10.23. $C_{10}H_6O_5NSNa$. Calculated %: Na 8.36.

1,2-Naphtho-(3',4')-furazan-4-sulfonic acid. 1) A solution of 6.55 g of 98% sodium hydroxide in 18 ml of water was added to a suspension of 13.77 g of the sodium salt of 1,2-naphthoquinonedioxime-4-sulfonic acid in 40 ml of water; the obtained solution was held for 1 hour at 15°, and then boiled for 15 minutes. After cooling, the sodium salt of naphthofurazansulfonic acid which was precipitated was filtered and washed with water and alcohol: the yield was 9.8 g (87%).

The sodium salt was quite soluble in water and was crystallized in the form of long colorless prisms. It contains 1/2 of a molecule of water of crystallization, which is not driven off at 160°.

5.430 mg sub.: 8.538 mg CO_2; 0.910 mg H_2O. 4.234 mg sub.: 0.365 ml N_2 (21°, 736 mm). 0.2268 g sub.: 0.0560 g Na_2SO_4. Found %: C 42.89; H 1.88; N 9.69; Na 8.00. $C_{10}H_5O_4N_2SNa \cdot 0.5H_2O$. Calculated %: C 42.71; H 2.15; N 9.96; Na 8.18.

The aniline salt is difficultly soluble in water and is crystallized in the form of thin colorless plates; m. p. is 277° (decomposes).

0.3684 g sub.: 10.74 ml 0.1 N $NaNO_2$. Found: M 343. $C_{16}H_{13}O_4N_3S$. Calculated: M 343.

The sulfochloride crystallizes in the form of cubic prisms (from benzene); m. p. 112.5-113.5°.

2) A suspension of 3 g of the sodium salt of naphthoquinonedioximesulfonic acid in 90 ml of acetic anhydride was boiled for 12 hours; the residue gradually grew lighter. The sodium salt of naphthofurazansulfonic acid which was precipitated was filtered and washed with water and methyl alcohol; the yield was 3.6 g. The m. p. found for the sulfochloride was 112.3 -113.5.

3) 8.6 g ml of 46.7% sodium hydroxide was added to a solution of 10.33 g of the sodium salt of the bisulfite compound of naphthofuroxane in 75 mm of water at 30°, and the mixture was boiled for 2 hours. The reaction product began to precipitate after only 10 minutes of boiling. After the cooling of the mixture, the residue of the sodium salt of naphthofurazansulfonic acid was filtered and washed with water and methyl alcohol; the yield was 5.17 g. Fractional evaporation of the filtrate separated 1.82 g more of the substance. The m. p. of the sulfochloride was 112.5-113.5°

The filtrate from the sodium salt of naphthofurazansulfonic acid, after the addition of water, was acidified with hydrochloric acid, and the residue of the sodium salt of 2-nitro-1-naphthol-4-sulfonic acid, which was precipitated, was then filtered; the yield was 0.73 g.

It crystallizes in the form of thin yellow plates (from water). The substance did not give reaction for 2-nitroso-1-naphthol-4-sulfonic acid, and on heating with nitric acid was converted into 2,4-dinitro-1-naphthol; on reduction with stannous chloride it converted into 2-amino-1-naphthol-4-sulfonic acid

The by-product which was formed by the action of soda on the bisulfite compound was crystallized from water in the form of long, colorless, prisms, and contained 7.99% sodium.

The m. p. of the sulfochloride was 112.8-113.5°.

1,2-Naphthofuroxane-4-sulfonic acid. 52 ml of 55.8% nitric acid was added to a suspension of 20.0 g of the sodium salt of 1,2-naphthoquinonedioxime-4-sulfonic acid in 100 ml of water at 20°; the mixture was held for 1 hour at 90° and for 15 minutes at 100°. After cooling the sodium salt of naphthofuroxanesulfonic acid was filtered, and washed with water and methyl alcohol; the yield was 14.0 g. On the neutralization of the filtrate with soda, 1.2 g more of the substance was separated. The total yield was 90.8%.

The sodium salt is difficultly soluble in water and is crystallized in the form of short colorless prisms; it does not contain water of crystallization.

6.312 mg sub.: 9.586 mg CO_2; 1.030 mg H_2O. 3.539 mg sub.: 0.311 ml N_2 (26°, 744 mm). 0.1900 g sub.: 0.0468 g Na_2SO_4. Found %: C 41.45; H 1.83; N 9.82; Na 7.97. $C_{10}H_5O_5N_2SNa$. Calculated %: C 41.67; H 1.75; N 9.72; Na 7.98.

1,2-Naphthalenediamine-4-sulfonic acid. 1) A solution of 18 g of crystalline 95% stannous chloride in 30 ml of 35.4% hydrochloric acid and 20 ml of water, was added to a solution of 5.18 g of the sodium salt of naphthoquinonedioximesulfonic acid in 50 ml of water, at 45°. The liquid, which becomes a yellow-brown color, was boiled for 10 minutes. On cooling, the residue of 1,2-naphthalenediamine-4-sulfonic acid was filtered; the yield after reprecipitation from a sodium acetate solution was 2.77 g. It crystallizes in the form of long prisms. With a bisulfite compound of phenanthrenequinone, it gives naphthophenanthrazinesulfonic acid (yellow needles), and on oxidation with nitric acid, it gives 1,2-naphthoquinone-4-sulfonic acid.

The sulfochloride of naphthoselenoidiazolesulfonic acid was prepared in the way that has been described previously [3]. It crystallized in the form of bipyramides (from chlorobenzene), m. p. 205-206°.

2) 0.5 g of crystalline stannous chloride was added to a solution of 2 g of the sodium salt of naphthofuroxanesulfonic acid in 150 ml of water at 80° after the latter solution had been acidified with 15 ml of 35.4% hydrochloric acid; 5.2 g of zinc powder was then added over the course of 25 minutes. The strongly frothing mass was stirred at 80° for 30 minutes and then cooled. The napththalenediaminesulfonic acid which was formed was filtered and

reprecipitated from a solution of sodium acetate; the yield was 1.47 g. On reduction with zinc in the absence of stannous chloride, the yield fell to 0.67 g.

The sulfochloride of naphthoselenodiazolesulfonic acid: m. p. 205-206°.

4-Chloro-1,2-naphthofuroxane. A solution of 2.94 g of potassium chlorate in 50 ml of water was added with stirring over the course of an hour to a boiling solution of 5.76 g of the sodium salt of 1,2-naphthofuroxane-4-sulfonic acid in 320 ml of water, which had been acidified with 11.2 ml of 35.5% hydrochloric acid. The reaction mixture was mixed while boiling for 1 hour, cooled, and the product of chlorination which was precipitated was filtered; the yield was 3.38 g, m. p. was 124-130°. The substance is quite soluble in acetic acid and alcohol, and crystallizes from alcohol in the form of curved needles which melt at 140.2-140.8°.

5.260 mg sub.: 10.520 mg CO_2; 1.136 mg H_2O; 0.852 mg Cl. 3.694 mg sub.: 0.402 ml N_2 (22°, 736 mm). Found %: C 54.56; H 2.42; Cl 16.19; N 12.20. $C_{10}H_5O_2N_2Cl$. Calculated %: C 54.44; H 2.28; Cl 16.07; N 12.71.

SUMMARY

1. The main product of the decomposition of the bisulfite compounds of naphthofuroxane by sodium hydroxide, first with cooling and then at room temperature, is 1,2-naphthoquinonedioxime-4-sulfonic acid. Naphthofuroxane, naphthofurazan and naphthofurazan-4-sulfonic acid are formed as by-products.

2. On the decomposition of the bisulfite compound by sodium hydroxide with heating naphthofurazan-4-sulfonic acid and a small amount of 2-nitro-1-naphthol-4-sulfonic acid are obtained.

3. 1,2-Naphthoquinonedioxime-4-sulfonic acid, on the action of hydrochloric acid is converted into 2-nitroso-1-naphthol-4-sulfonic acid, and on treatment with sodium hydroxide or acetic anhydride is converted into naphthofurazan-4-sulfonic acid; on reduction it is converted into 1,2-naphthalenediamine-4-sulfonic acid, and on oxidation with nitric acid into naphthofuroxane-4-sulfonic acid.

4. Naphthofuroxane-4-sulfonic acid, on the action of potassium chlorate and hydrochloric acid is converted into 4-chloronaphthofuroxane.

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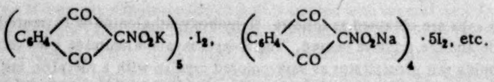
* T. p. = C. B. Translation pagination.

COMPLEX SALTS OF N-HYDROXYPHTHALONIMIDE WITH POLYIODIDES

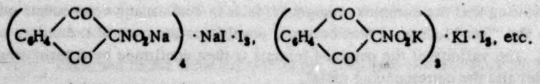
E. Vanag and G. Vanag

2-Nitro-1,3-indandione (I) is a pseudo hydrogen halide acid and its salts give crystalline complex salts with iodine [1, 2]. These compounds are not formed very easily and they lose iodine when exposed to the air. For example, depending on the preparation conditions, the following compounds were obtained:



$$\left(C_6H_4{<}^{CO}_{CO}{>}CNO_2K\right)_5\cdot I_2,\quad \left(C_6H_4{<}^{CO}_{CO}{>}CNO_2Na\right)_4\cdot 5I_2,\ \text{etc.}$$

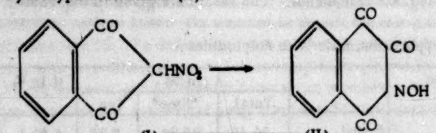
The ternary complexes are the most easily formed, i.e. those compounds in which the corresponding iodide is still retained, for example:



$$\left(C_6H_4{<}^{CO}_{CO}{>}CNO_2Na\right)_4\cdot NaI\cdot I_3,\quad \left(C_6H_4{<}^{CO}_{CO}{>}CNO_2K\right)_3\cdot KI\cdot I_3,\ \text{etc.}$$

These complexes also lose part of their iodine when exposed to the air. All of these complex salts are dark-colored crystalline substances with a bronze reflex.

It was recently shown by us [3, 4] that nitroindandione, under the influence of acid anhydrides and some other substances, is isomerized to N-hydroxyphthalonimide (II):

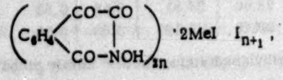


(I) (II)

The latter already fails to show the properties of a pseudo hydrogen halide acid; consequently, it was of interest to determine if the ability to form complexes with polyiodides was still retained. It was found that N-hydroxyphthalonimide is also very prone to such complex formation and that the resulting complexes are more stable than are the complex salts of the nitroindandione.

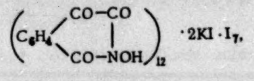
Fialkov and coworkers [5-10] have made a systematic study of the polyhalide type of complexes and come to the conclusion that compounds of a definite composition are frequently formed. Godina and Faerman [11], in studying the complexes of quinine sulfate with iodine, of which 7 are described in the literature, came to the conclusion that stoichiometrically determined ratios fail to exist between the amounts of iodine and hydroiodic acid, and that the amount of iodine entering into the composition of the polyhalide compounds is variable depends on the amount of excess iodine present at the time the compound is formed, and fails to obey stoichiometric rules. In all cases "adsorbed polyiodides" are formed, failing to represent stoichiometrically determined compounds.

As already mentioned, the salts of nitroindandione with iodine and polyiodides also have a variable composition depending on the preparation conditions. The composition of the complex salts of N-hydroxyphthalonimide proved to be independent of the amount of iodine in solution. In addition, it was found possible to depict the composition of many of the complex salts of N-hydroxyphthalonimide with metal polyiodides by the general formula:

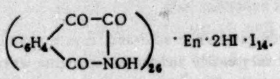


$$\left(C_6H_4{<}\begin{matrix}CO-CO\\ |\\ CO-NOH\end{matrix}\right)_{2n}\cdot 2MeI\ \ I_{n+1},$$

where: n – is a whole number, and Me – is a univalent cation. Thus, for example, the complex potassium salt has the composition:



where n, consequently, is equal to 6. The sodium and ammonium salts also have a similar composition. These salts are stable and fail to lose iodine when allowed to stand in the air. The freshly prepared complex salts of barium, strontium, calcium and nickel also correspond to the general formula, but on standing in the air they lose 1 atom of iodine. The ethylenediamine salt also corresponds to the general formula, where n = 13:



This salt fails to change when allowed to stand in air.

The complex salts are obtained as follows: N-hydroxyphthalonimide is treated with a solution of iodine in the corresponding iodide and the mixture heated. The N-hydroxyphthalonimide goes into solution, and from the solution on cooling the complex salt precipitates as dark-colored crystals with a metallic luster. The complex salts can be recrystallized from water, but in quite low yields, since the salt suffers partial decomposition when heated with water.

Having determined the total amount of iodine in the compound and the ratio of "free" iodine to iodide ion (I:I'), and knowing that the complex (compound) fails to contain any components other than N-hydroxyphthalonimide, metal iodide and "free" iodine, it then becomes possible on the basis of these data to calculate the composition of the complex. The validity of the obtained formula is then confirmed by determining the nitrogen (from the N-hydroxyphthalonimide) and the corresponding metal.

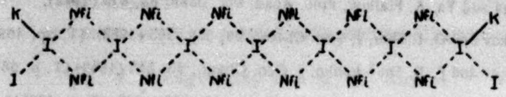
The salts were analyzed by the method developed by us for the analysis of the complex salts of nitroindandione [1, 2]. The active ("free") iodide was determined by titration with thiosulfate, the iodide ion by the Fajens titration method, and nitrogen by the micro Dumas method, and the corresponding cation by the general methods for the determination of metals in organic compounds. The results are given in the Table.

Complex Salts of N-Hydroxyphthalonimide With Polyiodides

Expt. No.	Salt composition		I (in %)			N in %	Cation in %	Condition of salt when Analyzed
			Total	"Free"	ion			
1	$(Nfi)_{12} \cdot 2NaI \cdot I_7$	Found	34.10	26.23	7.87	4.85	1.41	
		Calculated	32.83	25.54	7.30	4.83	1.32	
2	$(Nfi)_{12} \cdot 2KI \cdot I_7$	Found	33.49	25.91	7.58	4.71	2.30	
		Calculated	32.53	25.30	7.23	4.78	2.26	
3	$(Nfi)_{12} \cdot 2NH_4I \cdot I_7$	Found	33.79	25.79	8.00	5.52		
		Calculated	32.94	25.62	7.32	5.65		
4	$(Nfi)_{12} \cdot CaI_2 \cdot I_7$	Found	32.84	25.65	7.19	5.18		Fresh
		Calculated	32.90	25.59	7.31	4.83		
5	$(Nfi)_{10} \cdot SrI_2 \cdot I_5$	Found	30.71	22.30	8.35	5.40	2.34	
		Calculated	30.79	22.00	8.80	4.85	3.05	Aged
6	$(Nfi)_{12} \cdot BaI_2 \cdot I_7$	Found	31.24	24.24	7.00	4.91	3.75	
		Calculated	32.00	24.89	7.11	4.70	3.83	Fresh
7a	$(Nfi)_{12} \cdot NiI_2 \cdot I_7$	Found	32.38	25.14	7.14			
		Calculated	32.71	25.45	7.27			Fresh
7b	$(Nfi)_{12} \cdot NiI_2 \cdot I_6$	Found	29.82	22.57	7.25	5.28	1.64	
		Calculated	30.17	22.63	7.54	4.99	1.75	Aged
8	$(Nfi)_{10} \cdot ZnI_2 \cdot I_4$	Found	27.42	18.54	8.88	5.19		
		Calculated	27.84	18.57	9.30	5.11		Aged
9	$(Nfi)_{26} \cdot E_n \cdot 2HI \cdot I_{14}$	Found	28.00	24.51	3.48	5.53		
		Calculated	28.78	25.19	3.60	5.55		

Remarks: Nfi — N-hydroxyphthalonimide; En — ethylenediamine; fresh — freshly prepared; aged — allowed to stand in the air to constant weight.

As can be seen, the complex salts of N-hydroxyphthalonimide with polyiodides have a very complex composition. They can be classified as belonging to the group of multinuclear or "ultracomplex" compounds [12]. A closer study of their structure was not made. Purely schematically, for example, the potassium salt can be depicted as follows (Nfi = N-hydroxyphthalonimide):



EXPERIMENTAL

Potassium Salt. The N-hydroxyphthalonimide (0.5 g) is treated with several milliliters of a potassium iodide solution of iodine and the mixture heated until the N-hydroxyphthalonimide is completely dissolved and a transparent dark-brown solution is formed. On cooling, a precipitate of dark-colored plates with a metallic luster is obtained, uniformly permeating all of the liquid. The cooled mixture is suction filtered, washed with cold water, and dried at room temperature. The dry salt is removed from the filter paper as dark-colored pliant platelets. Yield 0.4 g. Its solubility in cold water is approximately 1 g per liter; the solution is brown-colored, and with starch it gives a blue coloration. It fails to give a precipitate with the ions of barium, strontium, calcium, nickel or copper; with silver and lead ions the precipitates of the corresponding iodides are obtained.

Sodium and Ammonium Salts. Obtained in the same manner as the potassium salt and fully comparable to it in their properties.

Barium Salt. Prepared the same as the potassium salt. Dark-colored crystals with a metallic reflex. On standing in the air for 3 weeks the salt lost 1 atom of iodine.

Strontium Salt. Prepared the same as the potassium salt. In external appearance it differs from the preceding salts; it fails to have the characteristic surface luster. On standing in the air the salt gradually loses iodine, for example, after 3 days the weight loss was 1%. To determine exactly the amount of iodine lost the salt was first dried in a desiccator over sulfuric acid in iodine vapors (an iodine crystal was placed in the desiccator), after which it was left in the open air. A month was required for the salt to establish a constant weight. The total weight loss was 2.93%; for the loss of 1 atom of iodine the theoretical weight loss should have been 3.28%.

Calcium Salt. Depending on the conditions variable precipitates were obtained – some as gels and others in the crystalline form. The composition of the freshly prepared crystalline salt corresponds to the general formula, while the gel, after its constant weight had been established, corresponds to the formula:

$$(\mathrm{Nfi})_{10} \cdot \mathrm{CaI_2} \cdot \mathrm{I_4}.$$

Nickel Salt. Prepared the same as the potassium salt. A crystalline precipitate with a greenish reflex. After 3 weeks in the air it loses 1 atom of iodine.

Zinc Salt. Prepared the same as the potassium salt. The yields were low. The crystals were not as well-formed as for the salts of the alkali metals, neither was the charactersitic surface luster present. In the air the salt loses iodine. In accord with the general formula the salt is minus 2 atoms of iodine. Due to the low yields the salt was not studied closer.

Ethylenediamine Salt. The ethylenediamine was dissolved in an equivalent amount of hydroiodic acid, the iodine was dissolved in the iodide solution thus obtained, and the N-hydroxyphthalonimide was treated in the usual manner with this solution. Dark-colored crystals were obtained, reminiscent of the complex salts of the alkali metals. The composition of the salt corresponds to the general formula.

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BORON FLUORIDE AS A CATALYST IN ORGANIC CHEMISTRY

X. ALKYLATION OF ANISOLE WITH PSEUDOBUTYLENE

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The alkylation of phenols with olefins in the presence of boron fluoride and its molecular compounds has been studied by a number of investigators. In our laboratory a study was made of the alkylation of phenols and the chlorophenols with pseudobutylene and 2-pentene in the presence of the boron fluoride-ethyl ether complex [1-3]. There are no original investigations on the alkylation of alkylphenyl ethers with olefins in the presence of boron trifluoride, and only a few patent communications exist. To accomplish this task we have made in recent years some systematic studies of the reaction between the alkylphenyl ethers and unsaturated compounds. In the present paper we describe the results obtained for the alkylation of anisole with pseudobutylene in the presence of $BF_3 \cdot O(C_2H_5)_2$, $BF_3 \cdot H_3PO_4$ and BF_3 with reactant ratios of 1:1, 1:2 and 1:2.5, and temperatures ranging from −5 to 100°.

As our studies revealed, the boron fluoride-ethyl ether complex, possessing high activity for the alkylation of phenol with pseudobutylene [1], proved to be but slightly effective for the above indicated reaction. Thus, anisole and pseudobutylene in the presence of 9% of $BF_3 \cdot O(C_2H_5)_2$, heated on the boiling water bath for 4 hours, give sec-butylanisoles in 24% of the theoretical yield. The extent of alkylation is almost nil when the amount of catalyst is reduced to 4%.

The compound of boron fluoride with orthophosphoric acid shows a higher catalytic activity. For example, if the reaction of gaseous pseudobutylene with anisole is carried out at room temperature in the presence of BF_3-saturated orthophosphoric acid, the sec-butylanisoles are obtained in 40% of the theoretical yield. Almost the same yield (37%) of alkylate is obtained if liquid pseudobutylene, anisole, and BF_3-saturated orthophosphoric acid are mixed at one time and the reaction mixture shaken for 8 hours at room temperature. Elevation of the temperature to 50 and 90°, but with the ratios of reactants and catalyst kept constant, increases the absorption rate of the pseudobutylene by the anisole and catalyst, the degree of alkylation is raised, and the sec-butylanisoles are obtained in 56% yield at 40-50° and a 66% yield at 80-90°.

Variation in the molar ratios of anisole to pseudobutylene from 1:1 to 1:2 and 1:2.5 also exerts a favorable influence on the reaction and gives a higher yield of alkylate for corresponding conditions.

Variation in the amount of BF_3 catalyst within the limits of 9 to 17% has very little effect on the degree of alkylation. However, a certain minimum exists for the boron fluoride, below which the degree of alkylation is greatly reduced. For example, a reduction in the amount of boron fluoride from 12 to 6% retards the absorption rate of the pseudobutylene by the anisole and $BF_3 \cdot H_3PO_4$ and reduces the yield of alkylate more than 2-fold (from 56 to 25%).

In contrast to the alkylation of aromatic hydrocarbons with olefins in the presence of $BF_3 \cdot H_3PO_4$, in the present reaction this catalyst and alkylate mix well and fail to separate on standing; for this reason the catalyst can only be used once.

When the alkylation of anisole with pseudobutylene is carried out in the presence of BF_3 alone, without the orthophosphoric acid, the absorption of pseudobutylene under comparable conditions (ratio of reactants 1:1, 16% of BF_3, and room temperature) is even better than in the presence of orthophosphoric acid, and the sec-butylanisoles are obtained in the same yield as when $BF_3 \cdot H_3PO_4$ is used. The use of larger amounts of BF_3, of the order of 25% to the total amount of reactants, gives an 82% yield of the alkylate, based on anisole. But under these conditions the alkylation is more profound and the exothermic heat developed during the time of pseudobutylene introduction raises the temperature of the reaction mixture to 60°. As a result the mono- and di-sec-butylanisoles are obtained in approximately equal amounts. Consequently, anhydrous orthophosphoric acid fails to exert any influence on the catalytic activity of boron fluoride in the given reaction, and for this reason the need to use it no longer exists. The use of boron fluoride without the phosphoric acid facilitates the isolation of the alkylation products, since on treating the reaction products with alkali an emulsion that separates into layers only after long standing is no longer formed. But the chief advantage here is the fact that up to 70% of the boron fluoride taken for reaction can be recovered by simple heating of the reaction mixture (prior to the alkali treatment) to 130-140°.

On the basis of the isolated products it can be concluded that in the alkylation of anisole with pseudobutylene in the pressure of 6-18% of BF_3 and its molecular compounds with H_3PO_4 and $O(C_2H_5)_2$ at temperatures of −5 to 100° a mixture of mono-sec-butylanisoles is mainly formed (75%), of which the chief component is o-sec-butylanisole. As a result, the alkylation proceeds first of all in the ortho-position.

EXPERIMENTAL

Reagents. The anisole used was the commercial freshly-distilled product with b. p. 150-152°, d_4^{17} 0.9972, n_D^{17} 1.5165. The pseudobutylene was isolated from a pseudobutylene-bivinyl (1,3-butadiene) fraction containing 60-80% of pseudobutylene.

Catalysts. The boron fluoride was obtained from CaF_2, B_2O_3 and concentrated H_2SO_4. The molecular compound of boron fluoride with orthophosphoric acid was obtained by saturating anhydrous orthophosphoric acid with boron fluoride until the weight increase corresponded to that of the compound $BF_3 \cdot H_3PO_4$; the substance was a clear, yellowish, viscous liquid and was used without previous distillation due to its ease of decomposition. The ethyl ether complex of boron fluoride was obtained by the passage of BF_3 into anhydrous ethyl ether, and after distilling off the excess ether, distilled at 124-127° as a colorless liquid that fumed easily in the air; it was used freshly distilled.

The alkylation of anisole with gaseous pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$ and BF_3 catalyst was run as follows: a weighed amount of anhydrous orthophosphoric acid was placed in a three-necked flask and to it was added BF_3 until the weight increase approximately corresponded to that of the compound $BF_3 \cdot H_3PO_4$. Anisole was then added to the prepared catalyst. In the reaction with BF_3 alone the anisole was first placed in the flask and then saturated with boron fluoride. The flask through its central opening was connected to a mechanical stirrer and was fitted with a mercury seal and reflux condenser, the latter being connected to a gasometer for collecting unreacted pseudobutylene. A thermometer was inserted in one of the side openings, and through the second opening, by means of a gas inlet tube reaching to the bottom of the reaction flask, a flask, filled with pseudobutylene and supplied with a stopcock, was connected. Then, with vigorous stirring, the pseudobutylene was passed into the anisole-catalyst mixture at a rate of 1.8 to 4.7 liters/hr., depending on the absorption intensity. At room temperature the pseudobutylene absorption was comparatively slight at the start, but after a certain induction period (in approximately 30-40 minutes after the start of pseudobutylene addition) the absorption rate rose sharply, and heating up of the reaction mixture was observed.

After adding a definite amount of pseudobutylene the stirring of the mixture was continued for another 2-6 hours. The alkylate and catalyst as a homogeneous liquid, of yellow color in the case of reaction at room temperature, and reddish-brown in the case of reaction at elevated temperature, was allowed to stand overnight at room temperature, after which it was diluted with a small amount of water (in the experiments with $BF_3 \cdot H_3PO_4$), the alkylate separated, treated with 5% soda solution, washed with water, dried over calcium chloride, and distilled. The unreacted anisole was removed by distillation at atmospheric pressure to 165°, while the residue was vacuum-distilled. The alkylate distilled almost completely. The residue from 15-40 g of alkylate subjected to fractionation was 0.2-2.0 g of heavy dark-brown oil. Such an oil from one of the experiments had d_4^{20} 1.010, n_D^{20} 1.5357. The fractions were collected in a boiling range of 25-30°. They were colorless oily liquids with a pleasant odor. In the experiments with BF_3 the reaction mixture, prior to neutralization with soda solution, was heated to 130-140°. The boron fluoride evolved here was passed into anhydrous ethyl ether. Then the alkylation products were treated as described above.

For the alkylation of anisole with liquid pseudobutylene in the presence of either $BF_3 \cdot O(C_2H_5)_2$ or $BF_3 \cdot H_3PO_4$ the anisole was placed in a wide test tube and the boron fluoride-ethyl ether complex was added, or anhydrous orthophosphoric acid was first placed in the test tube and saturated with boron fluoride, after which the anisole was added. The mixture of anisole and catalyst was cooled with an ice-salt mixture to −15°, the liquid pseudobutylene was added, the test tube was sealed, and then heated on the boiling water bath [in the experiments with $BF_3 \cdot O(C_2H_5)_2$] or allowed to stand at room temperature with periodic shaking (in the experiments with $BF_3 \cdot H_3PO_4$). The reaction products were isolated in exactly the same manner as in the experiments with gaseous pseudobutylene.

The most characteristic experiments on the alkylation of anisole with gaseous pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$ (Exps. 1-6) and with BF_3 (Exps. 9 and 10), and also with liquid pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$ (Exps. 7 and 8) and with $BF_3 \cdot O(C_2H_5)_2$ (Exps. 11 and 12), are given in the Table. In Exp. 9 the reaction mixture, after the passage of 13.2 g of pseudobutylene, was allowed to stand overnight at room temperature, after which it was gradually heated to 140°. The boron fluoride evolved here was passed into a receiver containing anhydrous ethyl ether. In this way there was obtained 8.92 g of $BF_3 \cdot O(C_2H_5)_2$, which calculated as free boron fluoride is 4.26 g (67.6%).

Identification of the Products. To identify the alkylation products the wide-boiling fractions collected in the primary distillation from each experiment (being a mixture of sec-butylanisoles), and having close boiling points, specific gravities and refractive indices, were combined and distilled through a fractionation column with an efficiency of 20-25 theoretical plates. The main reaction products were characterized by their physicochemical constants and by their oxidation with nitric acid to methoxyaromatic acids. Their structure was established on the basis of the obtained data. The oxidation was performed as follows: 0.2-0.25 g of the alkylation product was placed in a tube with 15-20 ml of 5% nitric acid. The tube was sealed and heated for 12-16 hours at 130-150°. After cooling the tube was opened, the obtained crystals filtered, and then recrystallized from hot water or ethyl alcohol. In this way the following sec-butylanisoles and methoxyaromatic acids were identified.

Alkylation of Anisole with Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$, BF_3 and $BF_3 \cdot O(C_2H_5)_2$

Exp. Nos.	Taken for Reaction (g)				% BF_3 on sum of reactants	Moles of pseudo-butylene per mole of anisole	Reaction conditions		Anisole recovered		Yield of alkylate	
	Anisole	pseudo-butylene	Catalyst				Temperature	Time of pseudo-butylene passage (Hrs.)	(g)	(%)	(g)	(%*)
			BF_3	H_3PO_4								
1	27.2	12.8	6.6	10.2	16.5	0.9	Room	3	11.65	42.83	14.85	39.63
2	27.0	17.5	5.5	9.5	12.4	1.2	45-50	4	9.00	33.33	23.20	56.57
3	27.0	16.5	6.4	9.5	14.7	1.2	80-90	1.5	8.33	30.85	26.90	65.59
4	27.1	28.0	3.3	4.8	6.0	2.0	Room	6	20.50	75.65	10.33	25.12
5	27.0	28.3	6.5	9.4	11.7	2.0	Room	4	14.60	54.07	22.93	55.91
6	21.6	28.0	6.5	9.4	13.1	2.5	Room	4	9.35	43.29	24.18	73.70
7	21.6	11.2	6.2	9.4	18.9	1.0	Room	8*	9.53	44.12	12.23	37.29
8	27.3	28.0	6.4	9.4	11.6	2.0	−5−0°	16**	25.10	91.94	3.75	9.04
9	27.0	13.2	6.3	–	15.7	0.9	Room	2	14.95	55.37	15.25	39.47
10	27.2	17.0	10.8	–	24.4	1.2	Room	1.5	6.45	23.71	34.05	82.42
			$BF_3 \cdot O(C_2H_5)_2$									
11	5.5	4.5	0.4		4.0	1.6	100°	16***	5.26	95.64	0.32	3.83
12	5.5	4.5	0.9		9.0	1.6	100°	4***	4.27	77.64	2.00	23.96

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* In Experiments 1 and 9 the alkylate yield was based on the pseudobutylene, in all of the other experiments – on the anisole.

** Shaking time for the reaction mixture.

*** Heating time.

o-sec-Butylanisole – colorless oily liquid with a pleasant odor. Its relative amount in the alkylate was 45.5%:

B. p. 76.5-78° (5 mm), d_4^{20} 0.9435, n_D^{20} 1.5029, MR_D 51.06; Calc. 51.20.
0.2066 g sub.: 24.29 g benzene: Δt 0.267°. Found: M 161.5. $C_{11}H_{16}O$. Calculated: M 164.1.

Oxidation with 5% HNO_3 by heating in a sealed tube for 14 hours at 140-150° gave an acid that was obtained as white needle stars or plates, from which o-methoxybenzoic acid with m. p. 101° was isolated by repeated recrystallization from hot water. From the literature, m. p. 98.5-99°.

p-sec-Butylanisole – colorless liquid with a pleasant odor. Its relative amount in the alkylate was 27.4%;

B. p. 81-83° (5 mm), d_4^{20} 0.9374, n_D^{20} 1.5000, MR_D 51.50; Calc. 51.20.
0.2224 g sub.: 23.11 g benzene: Δt 0.302°; 0.4147 g sub.: 23.11 g benzene: Δt 0.575°. Found: M 161.6, 158.2. $C_{11}H_{16}O$. Calculated: M 164.1.

Oxidation with 5% HNO_3 gave p-methoxybenzoic acid as white needles with m. p. 185-187° (from alcohol). From the literature, m. p. 184.2°.

2,4-Di-sec-butylanisole – colorless liquid with a pleasant odor. Its relative amount in the alkylate was 25.1%:

B. p. 129-132° (10 mm), d_4^{20} 0.9143, n_D^{20} 1.4940, MR_D 70.15; Calc. 69.75.
0.2023 g sub.: 23.56 g benzene: Δt 0.207°. 0.4124 g sub.: 23.56 g benzene: Δt 0.427°. Found: M 210.3, 207.9, $C_{15}H_{24}O$. Calculated: M 220.2.

Oxidation with 5% HNO_3 gave 4-methoxyisophthalic acid as white plates with m. p. 257-259° (melts with browning and sublimation).

SUMMARY

1. The alkylation of anisole with pseudobutylene was studied in the presence of the catalysts: BF_3, $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$, at temperatures ranging from −5 to 100°, and for various reactant ratios.

2. It was established that the most effective catalyst for the alkylation of anisole with pseudobutylene is BF_3, the use of which permits obtaining alkylation products in yields as high as 83%, and which can be recovered from the reaction mixture.

3. It was shown that orthophosphoric acid is not essential in the given reaction, and that the catalyst $BF_3 \cdot H_3PO_4$ fails to have any advantage over BF_3.

4. On the basis of the alkylation results it is assumed that anisole, under the studied conditions, is alkylated by pseudobutylene predominantly in the ortho-position.

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REACTION OF AMMONIA WITH 9,10-EPOXYELAIDIC ACID

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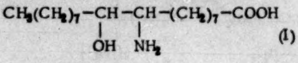
In the previous communication [1] we gave the results of studying the reaction between ammonia and 9,10-epoxyoleic acid; here, as was shown, 9-amino-10-hydroxystearic acid is formed.

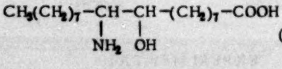
The present investigation is devoted to a study of the reaction between ammonia and 9,10-epoxyelaidic acid. The epoxyelaidic acid (m. p. 55-55.5°) was prepared by the oxidation of elaidic acid with acetyl hydroperoxide (peroxyacetic acid). The reaction of the epoxy compound with ammonia was run at 130°. A white product with m. p. 188-190° was isolated, which is soluble in dilute alkalies, acids, and in boiling isoamyl alcohol, and insoluble in water, ether, acetone, benzene and chloroform.

Its elementary analysis revealed that here we have a substance with the composition $C_{18}H_{37}O_3N$. The substance fails to evolve ammonia when treated with alkali. Oxidation with sodium periodate is accompanied by ammonia evolution. On the basis of the analysis data and the above-studied properties we concluded that we had obtained a hydroxyaminostearic acid with m. p. 188-190°, having the structure:



$$CH_3(CH_2)_7-\underset{OH}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH}}-(CH_2)_7-COOH \qquad (I)$$

or



$$CH_3(CH_2)_7-\underset{NH_2}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-(CH_2)_7-COOH \qquad (II)$$

Oxidation of this compound with lead tetraacetate gave pelargonaldehyde (nonanal) (semicarbazone, m. p. 98-100°). In addition to pelargonaldehyde a nitrogen-containing product was isolated, on hydrolysis giving azelaic acid with m. p. 105-106°. On the basis of its obtained oxidation products the hydroxyaminostearic acid should be assigned the structure of 9-amino-10-hydroxystearic acid (I).

For a more detailed study of the hydroxyaminostearic acid we synthesized a number of its derivatives. The hydrochloride, crystallizing as needles, had m. p. 144-145°. Apparently, the hydroxyaminostearic acid hydrochloride obtained by us is analogous to the hydrochloride (m. p. 143-144°) that was isolated by Egorov [2] when he treated oleic and elaidic acids with nitric oxides, followed by reduction with zinc in hydrochloric acid. Egorov failed to elucidate the structure of the compound obtained by him. It appeared sufficient proof to have the NO_2 group and the ester group (ONO) present in the compound. Also, the reduction product of the indicated compound was not studied.

In addition to the hydrochloride, we obtained the hydrochloride of the methyl ester as needles with m. p. 65-66°. The salt is readily soluble in alcohol and acetone, and poorly soluble in ether.

In its physical and chemical properties the indicated hydroxyaminostearic acid is quite different from its analog, obtained from epoxyoleic acid, which can readily be seen when the data given in the Table are compared.

In all probability, the indicated hydroxyaminostearic acids differs from each other in their spatial configuration. Due to the presence of two asymmetric carbon atoms it is possible for two racemic diastereomers to be formed, which, as we can see, differ sharply in their melting points, the same as the two dihydroxyacids. Apparently, the high-melting hydroxyaminostearic acid should be assigned the spatial configuration that corresponds to the OH and NH_2 groups being the greatest distance apart. The low-melting hydroxyaminostearic acid corresponds to that spatial configuration where the OH and NH_2 groups are found the closest to each other.

The reason for making such a conclusion is the fact that the low-melting acid (m. p. 154-155°), when reacted with nitrous acid, is converted into the dihydroxystearic acid with m. p. 100°. In accord with the study made by Esafov*, the formation of the acetone derivative is characteristic for the low-melting dihydroxystearic acid [3]. At

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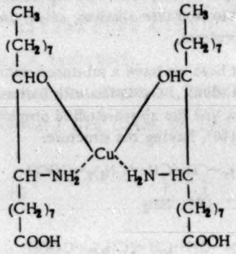
* We obtained analogous results when we repeated Esafov's experiments on the acetonation of the dihydroxystearic acids under identical conditions.

Compound	Melting points of the hydroxyaminostearic acids and their derivatives, obtained from the epoxy acid of	
	Oleic acid	Elaidic acid
Hydroxyaminostearic acid $C_{18}H_{37}O_3N$	154-155°	188-190°
$C_{18}H_{38}O_3NCl$ Hydrochloride	87-89	144-145
Hydrochloride of the methyl ester $C_{19}H_{40}O_3NCl$	61-62	65-66
Copper complex $C_{36}H_{72}O_6N_2Cu$	160-162 (with decomposition)	A complex is not formed

the same time the high-melting dihydroxystearic acid fails to show a tendency to form a similar compound. This postulation on the character of distribution of the OH and NH_2 groups in hydroxyaminostearic acids found its confirmation in the fact that the low-melting hydroxyamino acid gives a complex with copper, i.e. the hydroxy and amino groups are found in a more favorable position for formation of the five-membered ring. The high-melting hydroxyaminostearic acid, having the OH and NH_2 groups in the far position from each other, fails to give the copper complex.



EXPERIMENTAL

Preparation of Epoxyelaidic Acid. The epoxyelaidic acid was obtained by the oxidation of 85.3 g of elaidic acid, dissolved in 400 ml of ether, with an ether solution of acetyl hydroperoxide containing 5.2 g of active oxygen. After recrystallization from petroleum ether and alcohol the obtained epoxide melted at 55-55.5°. The epoxide yield was 95%. Its purity was determined by elementary analysis.

Found %: C 72.54, 72.48; H 11.66, 11.62. Calculated %: C 72.43; H 11.48.

Reaction of Ammonia with Epoxyelaidic Acid. A mixture of 2 g of the epoxide and 15 ml of 35% aqueous ammonia was heated in a sealed tube at 130° for 12 hours. The experiment was repeated 9 times. The ammonia was removed from the contents of the tubes, placed in a porcelain dish, first in the air, and then in vacuo. The obtained precipitate was filtered, washed with water, and then with alcohol and ether. The substance, obtained as a white powder, was insoluble in the ordinary solvents. It was treated at the boil with ethyl alcohol. From 18 g of epoxyelaidic acid there was obtained 18.7 g of hydroxyaminostearic acid. After recrystallization from isoamyl alcohol, m. p. 188-190°.

0.1060 g sub.: 0.2664 g CO_2; 0.1132 g H_2O. 0.0938 g sub.: 0.2354 g CO_2; 0.1008 g H_2O. 0.0669 g sub.: 3.06378 ml N_2. 0.0693 g sub.: 3.14139 ml N_2. 0.1058 g sub.: 0.01872 g KOH. 0.1065 g sub.: 0.01890 g KOH. Found %: C 68.54, 68.44; H 11.95, 12.02; N 4.58, 4.53. M 316.9, 316.1. $C_{18}H_{37}O_3N$. Calculated %: C 68.52; H 11.82; N 4.44. M 315.5.

Oxidation of the Substance with M. P. 188-190° by Sodium Periodate. To 0.04 g of the substance was added 2 ml of 1 N NaOH, 0.3 g of $NaIO_4$, and rapidly 10 ml of saturated K_2CO_3 solution. The liberated ammonia was removed by air-suction with heating to 60-70° for 40 minutes through a system consisting of two cylinders connected in series and containing 1 N hydrochloric acid. The total amount of nitrogen trapped was 1.0458 mg, which represents 59.7% of the theoretical required.

Oxidation with Lead Tetraacetate. To 11 g of hydroxyaminostearic acid in a round-bottomed flask, fitted with thermometer and reflux condenser, was added 90 ml of glacial acetic acid. Then to the acetic acid solution was added 16 g of lead tetraacetate and the mixture heated at 60° for 2 hours. On conclusion of heating the reaction mixture was diluted with 100 ml of water, and then steam-distilled. From 250 ml of distillate there was extracted 2.7 g of oily substance (54% of the theoretical). The test with fuchsin-sulfurous acid was positive. The Lassen reaction (for nitrogen) gave negative results. With semicarbazide hydrochloride the substance gives a semicarbazone, which after recrystallization from benzene and petroleum ether melted at 98-100°. Its mixed melting point with pelargonaldehyde semicarbazone failed to be depressed.

The residue in the flask (as a thick tar) was treated with steam, thoroughly washed with water, and dried. The substance failed to show the presence of an aldehyde group, but gave the characteristic reaction for nitrogen. The substance was hydrolyzed by heating on the water bath for 20 hours with 50 ml of a 2 N alcoholic potassium hydroxide solution. The copious evolution of ammonia was observed during the hydrolysis. On conclusion of reaction the alcohol was evaporated to dryness; the potassium salt was dissolved in water, neutralized with the calculated amount of dilute hydrochloric acid to slightly acid reaction, and extracted with ether. Removal of the ether gave a brown tarry mass as residue, from which a crystalline substance (2 g) was isolated by treatment with water under heating on the water bath. After recrystallization the substance had m. p. 105-106°. Its mixed melting point with azelaic acid failed to be depressed.

Preparation of the Hydrochloride $C_{18}H_{35}O_3NH_2 \cdot HCl$. To 3 g of the hydroxyaminostearic acid was added 10 ml of dilute hydrochloric acid, containing 0.36 g of HCl. The salt obtained in this manner was filtered and washed with cold water. The precipitate was recrystallized from ethyl acetate. Yield 85%. The salt crystallizes as needles. M. p. 144-145°.

0.2163 g sub.: 0.0878 g AgCl. 0.2158 g sub.: 0.0873 g AgCl. Found %: Cl 10.04, 10.01. $C_{18}H_{38}O_3NCl$. Calculated %: Cl 10.08.

Preparation of the Methyl Ester Hydrochloride $C_{19}H_{37}O_3NH_2 \cdot HCl$. A mixture of 5 g of the hydroxyaminostearic acid and 200 ml of anhydrous methyl alcohol, saturated with hydrogen chloride, in a round-bottomed flask with reflux condenser, was heated on the water bath for 2 hours. On conclusion of heating the hydrogen chloride and methyl alcohol were removed by vacuum-distillation (17 mm) at 16°. To achieve complete HCl removal the flask was treated three times with 50 ml portions of methyl alcohol, and each time the alcohol was removed by vacuum-distillation. The residue, dried over solid KOH in a vacuum-desiccator, became a crystalline mass after standing for two days. The latter, recrystallized from ethyl acetate, was obtained as fine needles with m. p. 65-66°. Yield 60%.

0.2049 g sub.: 0.0799 g AgCl. 0.2807 g sub.: 0.1100 g AgCl. Found %: Cl 9.65, 9.69. $C_{19}H_{40}O_3NCl$. Calculated %: Cl 9.69.

SUMMARY

The reaction of ammonia with epoxyelaidic acid leads to the formation of 9-amino-10-hydroxystearic acid (m. p. 188-190°), being the diastereoisomer (racemate) of the 9-amino-10-hydroxystearic acid (m. p. 154-155°) obtained from epoxyoleic acid. A number of derivatives, characterizing the properties of the hydroxyaminostearic acid, were prepared.

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SYNTHESIS OF THIAZOLIDONE DERIVATIVES WITH BIOLOGICAL INTEREST

I. COMPOUNDS OBTAINED FROM RHODANINE BY SUBSTITUTION IN THE THIO KETONE (THIONO) GROUP

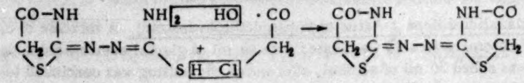
N. M. Turkevich and E. V. Vladzimirskaya

Compounds of 4-thiazolidone have acquired definite biological interest in recent years as substances possessing antithyroid and antitubercular activity. It is also possible that among them will be found compounds possessing anticonvulsant action, which compounds could replace diphenin and nirvanol. The high antithyroid activity established for thiourea [1], pseudohydantoin [2] and rhodanine [3] is associated with the presence of the grouping $>N-\underset{\underset{Y}{\|}}{C}-X-$, where X is sulfur, oxygen or the NH group, and Y is sulfur or the NH group. The indicated grouping is present [4] in the vinylthiooxazolidone molecule, which compound is a natural-occurring antithyroid factor found in the yellow turnip. The solitary 4-thiazolidone derivative found in nature is actithiazic acid [2-(5-carboxypentyl)-4-thiazolidone] (verified), which was isolated [5] as an antibiotic from a strain of stellated fungi (Streptomyces) (verified). Actithiazic acid exhibits high in vitro activity against Mycobacterium tuberculosis.

In this paper we present the synthesis of compounds obtained from rhodanine and containing in their molecules not only the thiazolidone nucleus (and with it also the grouping $>N-\underset{\underset{Y}{\|}}{C}-X-$, characteristic for antithyroid substances), but also the grouping $>C=\overset{|}{N}-\overset{|}{N}-C=$, characteristic [6] for preparations possessing antitubercular activity.

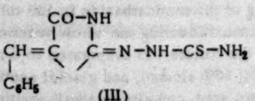
In our previous studies [7-9] it was shown that the $>CS$ group in the rhodanine molecule functions as a thio ketone and is incapable of conversion into the $\geqslant C-SH$ group, as a result of which rhodanine, analogous to ketones, is capable of forming the phenylhydrazone and oxime. Hydrogen sulfide is evolved when rhodanine is heated with an aqueous-alcohol solution of thiosemicarbazide and the previously unknown rhodanine thiosemicarbazone (I) is formed, which can be regarded as being a combination of pseudothiohydantoin and thiourea, i.e. of two substances possessing antithyroid activity.

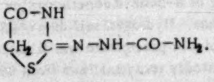
Using the reaction of Wilson and Burns [10], who were the first to show that thiosemicarbazones, analogous to thiourea, when condensed with α-halocarboxylic acids form pseudothiohydantoin derivatives, we attempted to convert rhodanine thiosemicarbazone into the azine. And actually, the condensation of this thiosemicarbazone with chloroacetic acid gave us the rhodanine azine (bis-pseudothiohydantoin) (II):


(I) (II)

Heating of the azine, and also of the rhodanine thiosemicarbazone, with concentrated hydrochloric acid gave the thiazolidinedione, which is proof for their proposed structures. The thiazolidine ring in molecules (I) and (II) is more stable than it is in the rhodanine molecule, since solutions of the former in NaOH fail to give the characteristic nitroprusside reaction.

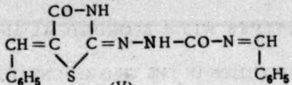
It is possible to obtain 5-benzylidenerhodanine thiosemicarbazone (III) by heating alcohol solutions of thiosemicarbazide and 5-benzylidenerhodanine, but its purification presents considerable difficulties.

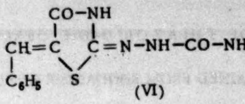

(III)

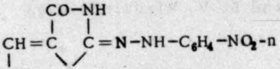

(IV)

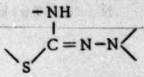
Rhodanine with semicarbazide under similar conditions forms rhodanine semicarbazone (IV), up to now obtained [11] in poor yield from chloroacetic acid and monothiohydrazocarboxamide (thioureidourea) $H_2NCSNHNHCONH_2$.

Condensation of the rhodanine semicarbazone with benzaldehyde gave us the dibenzylidene derivative (V). The same compound is also formed in the reaction of benzaldehyde with 5-benzylidenerhodanine semicarbazone (VI), the latter obtained by us in good yield from 5-benzylidenerhodanine and semicarbazide hydrochloride.


(V)


(VI)


(VII)


(VIII)

The condensation of 5-benzylidenerhodanine with p-nitrophenylhydrazine gave the p-nitrophenylhydrazone (VII), in which molecule, the same as in the chloromycetin molecule, a p-nitrophenyl group is present.

All of the compounds described by us can be regarded as being S-derivatives of the thiosemicarbazide (VIII) (it should be mentioned that the reaction of methyl iodide with thiosemicarbazide yields the S-methylthiosemicarbazide).

The preparations synthesized by us were investigated for their antimicrobial and physiological action. The studies made at the Cathedra of Histology of the Lvov Medical Institute revealed that rhodanine thiosemicarbazone possesses pronounced antithyroid action. It was found that in its degree of goiter production in white rats that rhodanine thiosemicarbazone is 20-25% more active than thiourea, and 10-15% more active than pseudothiohydantoin. The toxidity of the thiosemicarbazone with respect to white rats is slight.

EXPERIMENTAL

Rhodanine Thiosemicarbazone (2,4-Thiazolidinedione 2-Thiosemicarbazone). Ten grams of rhodanine was dissolved in a mixture of 70 ml of alcohol and 70 ml of water, after which it was heated with 10 g of potassium acetate and 7.8 g of thiosemicarbazide under reflux for 12 hours. Hydrogen sulfide was constantly evolved during the whole heating period. The clear solution with reddish tinge was evaporated on the water bath to small volume. The crystalline precipitate was filtered, thoroughly washed with water, and dried. The yield of yellow-orange crystalline powder was 12.3 g (86%). The compound is soluble in alkali solutions, ammonia, and in hot water, slightly soluble in alcohol, and insoluble in ether, acetic acid and benzene. M. p. 196-197° (from water).

20.5 mg sub.: 5.312 ml N_2 (20°, 737 mm). Found%: N 29.28. $C_4H_6ON_4S_2$. Calculated %: N 29.45.

The compound (0.1 g) was heated with 10 ml of concentrated hydrochloric acid on the water bath for 2 hours, after which the liquid was evaporated to small volume. The crystalline precipitate, filtered and then recrystallized from water, had m. p. 124-126° and corresponds to the thiozolidinedione [8].

Rhodanine Azine (2,4-Thiazolidinedione 2-Azine or Bispseudothiohydantoin). A mixture of 3.8 g of rhodanine thiosemicarbazone and 2.5 g of chloroacetic acid was heated with 30 ml of glacial acetic acid under reflux. After refluxing for 30 minutes there was added 50 ml of alcohol, after which the boiling was continued for another 3 hours. The crystalline precipitate was filtered, washed with boiling water, alcohol, ether, and dried. The yield of light-yellow product was 4.5 g (98%). The compound is insoluble in water, alcohol, ether, chloroform and benzene, soluble in alkali solutions and ammonia, and also in concd. HCl. Fails to melt below 300° [11]. Heating with concentrated hydrochloric acid gave the thiazolidinedione, m. p. 125°.

20.2 mg sub.: 4.297 ml N_2 (19°, 740 mm). Found %: N 24.21. $C_6H_6O_2N_4S_2$. Calculated %: N 24.33.

5-Benzylidenerhodanine Thiosemicarbazone (5-Benzyldiene-2,4-thialzolidinedione 2-Thiosemicarbazone). We obtained the 5-benzylidenerhodanine from chloroacetic acid, ammonium thiocyanate and benzaldehyde in one step [12]. A mixture of 5.5 g of 5-benzylidenerhodanine and 2.5 g of thiosemicarbazide in 100 ml of alcohol was heated under reflux for 24 hours. Hydrogen sulfide evolution was observed during the whole reaction period. The small amount of alcohol-insoluble precipitate was filtered, while the filtrate was evaporated to dryness on the water bath. The residue was repeatedly recrystallized from 96% alcohol, 50% alcohol, and glacial acetic acid. A yellow-orange substance was obtained, readily soluble in alcohol and acetic acid, and also in alkali solutions and ammonia, more difficultly soluble in chloroform, ether and benzene, and insoluble in water, and concentrated hydrochloric acid. M. p. 180-186°. Heating with concentrated hydrochloric acid gave the 5-benzylidenethiazolidinedione, m. p. 240° (from alcohol) [8].

22.1 mg sub.: 3.855 ml N_2 (20°, 740 mm). Found %: N 19.79. $C_{11}H_{10}ON_4S_2$. Calculated %: N 20.13.

Rhodanine Semicarbazone (2,4-Thiazolidinedione 2-Semicarbazone). A mixture of 10 g of rhodanine, 10 g of semicarbazide hydrochloride and 15 g of potassium acetate in 75 ml of water was heated under reflux for 15 hours. Here the constant evolution of hydrogen sulfide was observed. The originally homogeneous solution soon deposited a considerable amount of precipitate. After cooling the reaction mixture the precipitate was filtered and recrystallized from water. The yield of the semicarbazone as a white crystalline substance was 12.2 g (93%), soluble in alkali solutions and ammonia, and also in hot water and acetic acid, slightly soluble in alcohol, and insoluble in ether, chloroform and benzene. M. p. 222° with decomposition.

20.5 mg sub.: 5.834 ml N_2 (20°, 737 mm). Found %: N 32.15. $C_4H_6O_2N_4S$. Calculated %: N 32.19.

5-Benzylidenerhodanine Semicarbazone (5-Benzylidene-2,4-thiazolidinedione 2-Semicarbazone). A mixture of 4.4 g of 5-benzylidenerhodanine, 3 g of semicarbazide hydrochloride and 5 g of potassium acetate in 150 ml of alcohol was heated under reflux for 32 hours. Hydrogen sulfide was evolved during the whole reaction time. The boiling mixture was filtered, the precipitate washed with boiling alcohol, and then with water. The yield of yellow substance was 4.7 g (90%), insoluble in water, alcohol, ether, chloroform and benzene, soluble in alkali solutions and ammonia, and more difficultly soluble in acetic acid. M. p. 248° (from acetic acid).

21.0 mg sub.: 3.88 ml N_2 (19°, 739 mm). Found %: N 21.00. $C_{11}H_{10}O_2N_4S$. Calculated %: N 21.36.

5-Benzylidenerhodanine N^4-Benzylidenesemicarbazone (5-Benzylidene-2,4-thiazolidinedione 2-N^4-Benzylidenesemicarbazone). 1) A mixture of 0.52 g of 5-benzylidenerhodanine semicarbazone and 10 ml of benzaldehyde in 200 ml of anhydrous acetic acid was boiled under reflux for 4 hours. The reaction was accompanied by gradual dissolution of the originally insoluble starting substance. After cooling the reaction mixture the crystallized substance was filtered and then recrystallized from alcohol. The yield of substance, colorless with a yellowish tinge, was 0.55 g (80%), insoluble in water and concentrated hydrochloric acid, soluble on heating in alcohol, acetic acid, ether, chloroform, benzene, and alkali solutions. Fails to either melt or change when heated to 265°.

2) A mixture of 0.35 g of rhodanine semicarbazone and 10 ml of benzaldehyde in 200 ml of anhydrous acetic acid was heated at the boil, after which the procedure was the same as indicated above. The yield of substance, identical in its properties with the preceding, was 0.52 g (75%).

18.7 mg sub.: 2.675 ml N_2 (20°, 740 mm). Found %: N 16.23. $C_{18}H_{14}O_2H_4S$. Calculated %: N 15.99.

5-Benzylidenerhodanine p-Nitrophenylhydrazone (5-Benzylidene-2,4-thiazolidinedione 2-p-Nitrophenylhydrazone). A mixture of 1.4 g of the benzylidenerhodanine, 0.97 g of p-nitrophenylhydrazine and 3 g of potassium acetate in 50 ml of alcohol was heated under reflux for 10 hours. The evolution of hydrogen sulfide was observed during the whole reaction period. After cooling the reaction mixture the precipitate was filtered, washed with alcohol, and then water. The yield of dark-brown substance was 1.6 g (74%), insoluble in alcohol, ether, benzene, water and concentrated hydrochloric acid, and difficultly soluble in acetone, nitrobenzene, benzaldehyde and acetophenone. M. p. 233° (from nitrobenzene). The compound is soluble in alkalies and in soda solution with the formation of a red solution. When heated with sodium bicarbonate solution the compound also dissolves with the characteristic red coloration.

20.4 g mg sub.: 2.97 ml N_2 (22°, 740 mm). Found %: N 16.40. $C_{16}H_{12}O_3N_4S$. Calculated %: N 16.46.

SUMMARY

1. Thiosemicarbazide S-derivatives, having the thiazolidone nucleus in their molecule, can be obtained from rhodanine, which behaves like a typical ketone and gives condensation products with phenylhydrazine and its derivatives, hydroxylamine, semicarbazide and thiosemicarbazide.

2. The synthesis of the thiosemicarbazone, semicarbazone and azine of rhodanine was described, and also of the thiosemicarbazone, semicarbazone, benzylidenesemicarbazone and p-nitrophenylhydrazone of 5-benzylidenerhodanine.

3. All of the described substances show acidic properties and are soluble in alkali solutions.

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SYNTHESIS AND PHYSIOLOGICAL EFFECT ON PLANTS OF SOME β-ARYLOXYETHANOLS AND ARYLOXYACETONES

K. S. Bokarev and N. N. Melnikov

In recent years diverse aryloxyalkylcarboxylic acids and their various derivatives have found quite extensive use as chemical weed-control agents and plant growth stimulants [1-6]. Up to now a large number of this type of substances have been synthesized and described [7-10]. However, compounds of the general formula ArOR, containing in the aliphatic radical not the carboxyl, but other functional groups, such as hydroxyl, carbonyl groups, etc., have been described in limited number only and their systematic study has not been made. At the present time the only aryloxyethanols described are the 2- and 3-methoxyphenoxyethanols, 4-bromophenoxyethanol, 2,4-dichlorophenoxyethanol, 2,4,6-tribromophenoxyethanol, pentachlorophenoxyethanol, the 1- and 2-naphthyloxyethanols, 2-chlorophenoxyethanol, 4-chlorophenoxyethanol and phenoxyethanol [11-32], while of the aryloxyacetones the only compounds described in the literature are the phenoxy-, 4-chlorophenoxy-, 4-bromophenoxy-, 2-methoxyphenoxy-, 4-methoxyphenoxy-, 4-ethoxyphenoxy-, 4-propoxyphenoxy-, 4-butoxyphenoxy-, 2,4-dichlorophenoxy-, 2,4,6-tribromophenoxy- and naphthyloxyacetones [33-48].

Together with this a systematic study of these groups of compounds is of interest, both for the accumulation of material on the relationship existing between the physiological action of organic compounds on plants and their structure, and also for obtaining knowledge on the mechanism of their action. In accord with this we synthesized a number of aryloxyethanols and aryloxyacetones, containing various functional groups in the aromatic radical. We obtained the aryloxyethanols and arylmercaptoethanols by the reaction of sodium phenolates or mercaptides with ethylene chlorohydrin:

$$\mathrm{ArXNa + ClCH_2CH_2OH \rightarrow ArXCH_2CH_2OH + NaCl},$$

where X = O or S.

The aryloxy- and arylmercaptoethanols synthesized by us and their properties are given in Table 1. Some of the aryloxyethanols were identified by us as the α-naphthylcarbamates (1-naphthalenecarbamates) (Table 2).

The aryloxyethanols as 5% kaolin dusts were tested as germination inhibitors on radishes and flax. Of the investigated compounds the most active proved to be: 2,4-dichlorophenoxyethanol, 2,4,5-trichlorophenoxyethanol, 4-bromophenoxyethanol and 2-naphthyloxyethanol. The pentachlorophenoxyethanol and 2,4,6-tribromophenoxyethanol proved to be considerably less active. The 2-alkoxy-4,5-dihalophenoxyethanols possessed low activity, while the 4-alkoxy-2-halophenoxyethanols, alkoxyphenoxyethanols and 1-naphthyloxyethanol were completely inactive.

The aryloxyacetones and arylmercaptoacetones were synthesized by the reaction of bromoacetone with the corresponding phenolates or mercaptides in aqueous acetone solution.

$$\mathrm{ArXNa + BrCH_2COCH_3 \rightarrow ArXCH_2COCH_3 + NaBr},$$

where X = O or S.

The compounds obtained by us and their properties are given in Table 3. The properties of the corresponding semicarbazones are given in Table 4. The testing of the aryloxyacetones for the germination inhibition of radish and hemp seeds revealed that these compounds are practically without activity.

It appears of interest to study these compounds as antagonists literature that such properties are present in 2,4-dichlorophenoxyanisole and some other compounds, containing ether groupings [49].

A comparison of the physiological effect on plants of the aryloxyacetic acids, aryloxyethanols and aryloxyacetones, all containing the same aromatic radicals, reveals that the acids are the most active compounds and the aryloxyacetones the least active.

TABLE 1

β-Aryloxyethanols and Their Properties

Expt. Nos.	Name and formula	Taken for reaction				Yield		Solvent for Recrystallization	Melting point	Boiling point	d_4^{20}	n_D^{20}	Literature data	Analysis			
		Phenol (g/mole)	$ClCH_2CH_2OH$ (g/mole)	NaOH (g/mole)	Water (in ml)	(in g)	(in %)							Weight (in g)	0.1 N $AgNO_3$ required for titration (in ml)	Halogen found (in %)	Halogen calculated (in %)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	4-Bromophenoxyethanol $BrC_6H_4OCH_2CH_2OH$	$\frac{21}{0.121}$	$\frac{10}{0.125}$	$\frac{4.85}{0.121}$	20	13.9	52.9	Gasoline (b.p. 100-125°)	55°	147-149° (2 mm)	—	—	*	0.2201 0.2356	10.17 10.87	36.93 36.87	36.82
2	2,4-Dichlorophenoxyethanol $Cl_2C_6H_3OCH_2CH_2OH$	$\frac{163}{1}$	$\frac{88}{1}$	$\frac{44}{1}$	300	110	53.2	Benzene	58	185-190 (100 mm)			**	0.1895 0.1761	18.52 17.12	34.65 34.47	34.25
3	2,4,5-Trichlorophenoxyethanol $Cl_3C_6H_2OCH_2CH_2OH$	$\frac{197.5}{1}$	$\frac{80.5}{1}$	$\frac{40}{1}$	500	230.6	80	Gasoline	65					0.1162 0.0918	14.45 11.46	44.08 44.26	44.04
4	2-Methoxyphenoxyethanol $CH_3OC_6H_4OCH_2CH_2OH$	$\frac{37.2}{0.3}$	$\frac{26.6}{0.33}$	$\frac{12}{0.3}$	40	31.7	62.3			163-164 (15 mm)	1.1561	1.5439	***				
5	3-Methoxyphenoxyethanol $CH_3OC_6H_4OCH_2CH_2OH$	$\frac{37.2}{0.3}$	$\frac{26.6}{0.33}$	$\frac{12}{0.3}$	40	39.7	79			143 (5 mm)	1.1531	1.5416	****				
6	2-Ethoxyphenoxyethanol $C_2H_5OC_6H_4OCH_2CH_2OH$	$\frac{31.4}{0.227}$	$\frac{28.2}{0.35}$	$\frac{9.1}{0.227}$	40	23.9	65	Gasoline	38-39	128-130 (2 mm)							
7	3-Propoxyphenoxyethanol $C_3H_7OC_6H_4OCH_2CH_2OH$	$\frac{12.2}{0.0803}$	$\frac{6.8}{0.085}$	$\frac{3.2}{0.0803}$	20	13	83			157 (3 mm)	1.0867	1.5240					
8	4-Propoxyphenoxyethanol $C_3H_7OC_6H_4OCH_2CH_2OH$	$\frac{19.7}{0.13}$	$\frac{11.3}{0.14}$	$\frac{5.2}{0.13}$	40	18.2	70.5	Gasoline and CCl_4	75								
9	3-Butoxyphenoxyethanol $C_4H_9OC_6H_4OCH_2CH_2OH$	$\frac{13.4}{0.08}$	$\frac{6.8}{0.085}$	$\frac{3.2}{0.08}$	20	15.6	84.3			170-172 (5 mm)	1.0591	1.5197					

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* M. p. 49-50° [15], 55° [24].

** M. p. 57-58° [27].

*** B. p. 166-167° (22 mm) [13].

**** B. p. 153° (14 mm) [16], 160° (2 mm) [22].

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	133	14	15	16	17	18
10	4-Propoxy-2-chlorophenoxyethanol $C_3H_7O(Cl)C_6H_3OCH_2CH_2OH$	$\frac{25.7}{0.155}$	$\frac{12.9}{0.16}$	$\frac{6.2}{0.155}$	40	18.4	51.7			169-171 (2 mm)	1.1920	1.5367		0.2642 0.1425	11.54 6.41	15.48 15.60	14.57
11	4-Butoxy-2-chlorophenoxyethanol $C_4H_9O(Cl)C_6H_3OCH_2CH_2OH$	$\frac{30.5}{0.153}$	$\frac{12.2}{0.153}$	$\frac{6.43}{0.153}$	40	24	64.5			171-172 (3 mm)	1.1631	1.5309		0.1711 0.1920	7.02 7.78	14.55 14.38	14.49
12	4-Isopentyloxy-2-chlorophenoxyethanol $C_5H_{11}O(Cl)C_6H_3OCH_2CH_2OH$	$\frac{16}{0.075}$	$\frac{6.5}{0.08}$	$\frac{3}{0.075}$	20	12.5	64.8			191-194 (6 mm)	1.1319	1.5241		0.1632 0.1314	6.50 5.05	13.72 13.63	13.70
13	4-Butoxy-2-bromophenoxyethanol $C_4H_9O(Br)C_6H_3OCH_2CH_2OH$	$\frac{27}{0.11}$	$\frac{9.7}{0.12}$	$\frac{4.4}{0.11}$	40	22	69.2			200-202 (9 mm)	1.3242	1.5433		0.1949 0.2084	6.69 7.18	27.42 27.52	27.64
14	2-Methoxy-4,5-dichlorophenoxyethanol $CH_3O(Cl_2)C_6H_2OCH_2CH_2OH$	$\frac{11.8}{0.06}$	$\frac{5.6}{0.07}$	$\frac{2.44}{0.06}$	20	9.6	66.7	Mixture of gasoline, dichloroethane and CCl_4	94					0.1053 0.1171	8.86 9.95	29.82 30.12	29.91
15	2-Ethoxy-4,5-dichlorophenoxyethanol $C_2H_5O(Cl_2)C_6H_2OCH_2CH_2OH$	$\frac{13.5}{0.0652}$	$\frac{5.6}{0.07}$	$\frac{2.6}{0.0652}$	20	8.2	44.8	Gasoline and CCl_4	77					0.1685 0.1908	13.39 15.35	28.18 28.53	28.24
16	2-Propoxy-4,5-dichlorophenoxyethanol $C_3H_7O(Cl_2)C_6H_2OCH_2CH_2OH$	$\frac{33}{0.15}$	$\frac{13}{0.16}$	$\frac{6}{0.15}$	20	32	73	Dichloroethane and CCl_4	55	177-179 (2 mm)				0.1307 0.1852	9.95 13.71	26.99 26.25	26.75
17	2-Butoxy-4,5-dichlorophenoxyethanol $C_4H_9O(Cl_2)C_6H_2OCH_2CH_2OH$	$\frac{24.9}{0.106}$	$\frac{8.8}{0.11}$	$\frac{4.12}{0.106}$	40	20.5	71.2			180-182 (5 mm)	1.2529	1.5460		0.1668 0.1738	12.09 12.41	25.71 25.31	25.40
18	2-Isopentyloxy-4,5-dichlorophenoxyethanol $C_5H_{11}O(Cl_2)C_6H_2OCH_2CH_2OH$	$\frac{24.9}{0.1}$	$\frac{8.8}{0.11}$	$\frac{4}{0.1}$	40	18.4	62.8			149-152 (2 mm)	1.1918	1.5350		0.2259 0.1801	15.48 12.25	24.30 24.12	24.19
19	2-Methoxy-4,5-dibromophenoxyethanol $CH_3O(Br_2)C_6H_2OCH_2CH_2OH$	$\frac{28.2}{0.1}$	$\frac{8.8}{0.11}$	$\frac{4}{0.1}$	40	23.4	71.8	Mixture of gasoline, dichloroethane and CCl_4	112					0.3264 0.2133	20.18 13.05	49.40 48.91	49.03

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
20	2-Ethoxy-4,5-dibromophenoxyethanol $C_2H_5O(Br_2)C_6H_2OCH_2CH_2OH$	$\frac{29.6}{0.1}$	$\frac{8.8}{0.11}$	$\frac{4}{0.1}$	40	19.4	57	Gasoline and CCl_4	88					0.2573 0.2161	15.07 12.68	46.80 46.91	47.00
21	2-Propoxy-4,5-dibromophenoxyethanol $C_3H_7O(Br_2)C_6H_2OCH_2CH_2OH$	$\frac{26}{0.084}$	$\frac{6.9}{0.85}$	$\frac{3.4}{0.085}$	40	23.4	79.7	Gasoline and CCl_4	64-65					0.2718 0.1725	15.34 9.84	45.09 45.56	45.14
22	2-Butoxy-4,5-dibromophenoxyethanol $C_4H_9O(Br_2)C_6H_2OCH_2CH_2OH$	$\frac{30.5}{0.0941}$	$\frac{7.65}{0.095}$	$\frac{3.76}{0.0941}$	40	18.53	52	Gasoline and CCl_4	53-54	202-204° (6 mm)				0.1278 0.1311	6.93 7.10	43.35 43.28	43.42
23	2-Isophentyloxy-4,5-dibromophenoxyethanol $C_4H_9O(Br_2)C_6H_2OCH_2CH_2OH$	$\frac{29.6}{0.0873}$	$\frac{8}{0.1}$	$\frac{3.5}{0.0873}$	40	15.3	45.6			180-182 (3 mm)	1.1508	1.5275		0.1213 0.1524	6.46 8.12	42.43 42.57	42.61
24	β-Naphthylmercaptoethanol $C_{10}H_7SCH_2CH_2OH$	$\frac{40}{0.25}$	$\frac{18}{0.255}$	$\frac{10}{0.25}$	500	26.8	52.5	Gasoline	55-56	220-230 (3 mm)				0.1590 0.1125	0.1772* 0.1266*	15.31** 1545**	15.69**

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* Found $BaSO_4$ (in g).

** Amount of S indicated (in %).

EXPERIMENTAL

Preparation of Aryloxyethanols. The aryloxyethanols were prepared under the following conditions. The phenol under heating was dissolved in aqueous sodium hydroxide solution. After the phenol had dissolved, to the heated solution was gradually added ethylene chlorohydrin, and the reaction mixture was boiled under reflux for 2 hours. To the reaction mixture after cooling was added 30-50 ml of 5% sodium hydroxide solution, and the aryloxyethanol was extracted with dichloroethane. The dichloroethane extract was washed with water and dried over anhydrous magnesium sulfate. After distilling off the solvent the residue was either vacuum-distilled or recrystallized from a suitable solvent. The 1-Naphthalenecarbamic acid esters were prepared as follows: equimolar amounts of the alcohol and 1-naphthyl isocyanate were heated for 5-10 minutes on the boiling water bath. The substance obtained after cooling was recrystallized from a suitable solvent and analyzed for its nitrogen content.

Preparation of Aryloxyacetones. To a solution of 0.2 mole of the phenol in 20-40 ml of acetone was added 0.1-0.2 mole of bromoacetone, and then with good stirring was gradually added a solution of 0.1 mole of sodium hydroxide in 20-40 ml of water. After all of the sodium hydroxide had been added the reaction mixture was boiled in a flask under reflux for 10-20 hours. A mechanical stirrer was used to vigorously stir the reaction mixture during the whole reaction time. On conclusion of reaction the mixture was cooled, to it was added 200 ml of 5% aqueous sodium hydroxide solution, and the reaction product was extracted with benzene. The benzene solution was dried over anhydrous magnesium sulfate, and the benzene removed by distillation. The residue was either vacuum-distilled or recrystallized from a suitable solvent. The semicarbazones of the obtained ketones were synthesized in the usual manner.

TABLE 2

Properties of Aryloxyethanol Esters of 1-Naphthalenecarbamic Acid

Expt. Nos.	Name and formula of the 1-Naphthalenecarbamic Acid Ester	Melting Point	Solvent for Recrystallization	Analysis			
				Weight (in g)	0.1 N H_2SO_4 required for titration (in ml)	Found N (in %)	Calculated N (in %)
1	α-Naphthyloxyethyl $C_{23}H_{19}O_3N$	131-132°	Dichloroethane and benzene	0.1358 0.1684	4.01 4.89	4.14 4.06	3.92
2	β-Naphthyloxyethyl $C_{23}H_{19}O_3N$	152	Dichloroethane and benzene	0.1475 0.1248	4.32 3.63	4.10 4.08	3.92
3	2-Methoxyphenoxyethyl $C_{20}H_{19}O_4N$	137-138	Benzene	0.1791 0.2162	5.28 6.29	4.13 4.07	4.15
4	3-Methoxyphenoxyethyl $C_{20}H_{19}O_4N$	107-108	Mixture of benzene with dichloroethane and benzene	0.1460 0.1614	4.43 4.96	4.25 4.30	4.15
5	2-Ethoxyphenoxyethyl $C_{21}H_{21}O_4N$	131-132	Benzene	0.1721 0.1799	4.94 4.95	4.02 3.86	3.99
6	3-Propoxyphenoxyethyl $C_{22}H_{23}O_4N$	120-121	Benzene	0.1424 0.1365	4.17 3.98	4.10 4.08	3.83
7	4-Propoxyphenoxyethyl $C_{22}H_{23}O_4N$	104	Gasoline	0.1404 0.1419	3.93 3.77	3.92 3.72	3.83
8	3-Butoxyphenoxyethyl- $C_{23}H_{25}O_4N$	116-117	Mixture of gasoline with benzene	0.1644 0.1757	4.32 4.72	3.68 3.77	3.69

TABLE 3

Aryloxyacetones and their Properties

Expt. Nos.	Name and Formula	Taken for Reaction (g/mole)			Solvent	Yield	
		Phenol	$BrCH_2COCH_3$	NaOH		(in g)	(in %)
1	2-Chlorophenoxyacetone $ClC_6H_4OCH_2COCH_3$	$\frac{44.5}{0.344}$	$\frac{24.7}{0.18}$	$\frac{7.2}{0.18}$	Acetone and water	15	45
2	4-Chlorophenoxyacetone $ClC_6H_4OCH_2COCH_3$	$\frac{25.7}{0.2}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	The same	11.2	60.5
3	2,4-Dichlorophenoxyacetone $Cl_2C_6H_3OCH_2COCH_3$	$\frac{32.6}{0.2}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	11.8	54
4	2,4,5-Trichlorophenoxyacetone $Cl_3C_6H_2OCH_2COCH_3$	$\frac{19.75}{0.1}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	14.5	57.3
5	Pentachlorophenoxyacetone $Cl_5C_6OCH_2COCH_3$	$\frac{26.6}{0.1}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	24.5	80
6	2-Bromophenoxyacetone $BrC_6H_4OCH_2COCH_3$	$\frac{26}{0.11}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	11.5	50.2
7	4-Propoxy-2-chlorophenoxyacetone $C_3H_7O(Cl)C_6H_3OCH_2COCH_3$	$\frac{27.8}{0.15}$	$\frac{20.6}{0.15}$	$\frac{6}{0.15}$	" "	17.4	51
8	4-Butoxy-2-chlorophenoxyacetone $C_4H_9O(Cl)C_6H_3OCH_2COCH_3$	$\frac{22.1}{0.114}$	$\frac{15.6}{0.114}$	$\frac{4.5}{0.114}$	" "	13.6	49
9	2-Ethoxy-4,5-dichlorophenoxyacetone $C_2H_5O(Cl_2)C_6H_2OCH_2COCH_3$	$\frac{10.3}{0.05}$	$\frac{6.85}{0.05}$	$\frac{2}{0.05}$	" "	9.6	73.6
10	2-Butoxy-4,5-dichlorophenoxyacetone $C_4H_9O(Cl_2)C_6H_2OCH_2COCH_3$	$\frac{11.75}{0.05}$	$\frac{6.85}{0.05}$	$\frac{2}{0.05}$	" "	7.7	52.9
11	2-Methoxy-4,5-dibromophenoxyacetone $CH_3O(Br_2)C_6H_2OCH_2COCH_3$	$\frac{28.2}{0.1}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	23.1	68.3
12	2-Ethoxy-4,5-dibromophenoxyacetone $C_2H_5O(Br_2)C_6H_2OCG_2COCH_3$	$\frac{29.6}{0.1}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	19.7	55.6
13	2-Propoxy-4,5-dibromophenoxyacetone $C_3H_7O(Br_2)C_6H_2OCH_2COCH_3$	$\frac{22.6}{0.1}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	25.5	94.5
14	2-Butoxy-4,5-dibromophenoxyacetone $C_4H_9O(Br_2)C_6H_2OCH_2COCH_3$	$\frac{16.2}{0.05}$	$\frac{6.85}{0.05}$	$\frac{2}{0.05}$	" "	15.5	81.7
15	2-Isopentyloxy-4,5-dibromophenoxyacetone $C_5H_{11}O(Br_2)C_6H_2OCH_2COCH_3$	$\frac{16.9}{0.05}$	$\frac{6.85}{0.05}$	$\frac{2}{0.05}$	" "	14.5	73.6
16	β-Naphthylmercaptoacetone $C_{10}H_7SCH_2COCH_3$	$\frac{16}{0.1}$	$\frac{13.7}{0.1}$	$\frac{4}{0.1}$	" "	17.1	79.6

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* Found $BaSO_4$ (in g).

** Amount of S indicated (in %).

Solvent for Recrystallization	Melting point	Boiling point	Literature data	Analysis			
				Weight (in g)	0.1 N AgNO$_3$ required for titration (in ml)	Found Halogen (in %)	Calculated Halogen (in %)
		110-115° (4 mm)		0.1537 0.1125	8.40 6.08	19.05 19.17	19.21
Gasoline	57°	168-170 (20 mm)	B.p. 147-148° (17 mm [45]	0.1591 0.1911	8.53 10.3	19.01 19.11	19.21
Gasoline	54	138-141 (4 mm)	M.p. 54-55° [46], 55.5-56.5° [47]	0.3069 0.2664	27.94 24.16	32.28 32.15	32.37
Mixture of gasoline and benzene	116			0.1479 0.1136	17.50 13.56	41.92 42.32	41.96
Methyl alcohol and gasoline	105-105.5		M.p.106.5 107° [47]	0.2305 0.2406	35.70 36.48	54.91 54.85	54.99
		150-155 (10 mm)		0.1524 0.2523	6.61 10.98	34.67 34.79	34.88
Gasoline	50	170-172 (3 mm)		0.3404 0.5262	13.75 21.39	14.32 14.42	14.61
		174-175 (3 mm)		0.2164 0.2350	8.61 9.29	14.10 14.02	13.81
Gasoline and CCl$_4$	54	-		0.1566 0.2030	11.95 15.30	27.06 26.74	26.95
Gasoline	69	155-158 (3 mm)		0.1339 0.1911	9.26 13.16	24.51 24.42	24.35
CCl$_4$ and a mixture of gasoline with dichloroethane	110			0.2499 0.3429	14.75 20.24	47.18 47.16	47.28
Gasoline and CCl$_4$	72			0.1283 0.1439	7.26 8.16	45.25 45.30	45.40
Gasoline and dilute methyl alcohol	71			0.2464 0.1442	13.39 7.84	43.42 43.45	43.66
Gasoline and CCl$_4$	61			0.1284 0.1674	6.78 8.80	42.21 42.01	42.05
		198-200 (3 mm)		0.3050 0.2456	15.54 12.50	40.71 40.68	40.55
Gasoline and methyl alcohol	135			0.0390 0.0438	0.0417* 0.0465*	14.70** 14.58**	14.82**

TABLE 4

Properties of the Semicarbazones of Aryloxyacetones and Arylmercaptoacetones

Expt. Nos.	Semicarbazone	Melting point	Analysis			
			Weight (in g)	0.1 N $AgNO_3$ required for titration (in ml)	Found halogen (in %)	Calculated halogen (in %)
1	2-Chlorophenoxyacetone	171*	0.1290	5.35	14.72	14.67
	$C_{10}H_{12}O_2N_3Cl$		0.2417	10.12	14.85	
2	4-Chlorophenoxyacetone	181-182	0.1107	4.50	14.45	14.67
	$C_{10}H_{12}O_2N_3Cl$		0.1136	4.67	14.58	
3	2,4-Dichlorophenoxyacetone	184-185*	0.0464	3.34	25.52	25.68
	$C_{10}H_{11}O_2N_3Cl_2$		0.1061	7.59	25.37	
4	2,4,5-Trichlorophenoxyacetone	202	0.1381	13.21	33.93	34.25
	$C_{10}H_{10}O_2N_3Cl_3$		0.1570	15.03	33.94	
5	Pentachlorophenoxyacetone	193-194	0.0876	12.01	48.63	48.78
	$C_{10}H_8O_2N_3Cl_5$	(decomp.)	0.0737	10.12	48.69	
6	2-Bromophenoxyacetone	150-151	0.0847	2.96	27.94	27.93
	$C_{10}H_{12}O_2N_3Br$		0.0372	1.29	27.75	
7	4-Bromophenoxyacetone	197**	0.0516	1.80	27.87	27.93
	$C_{10}H_{12}O_2N_3Br$		0.0466	1.63	27.97	
8	2,4,6-Tribromophenoxyacetone	196.5	0.0497	3.35	53.91	54.00
	$C_{10}H_{10}O_2N_3Br_3$		0.0812	5.47	53.85	
9	4-Propoxy-2-chlorophenoxyacetone	147	0.1704	5.04	12.15	11.83
	$C_{13}H_{18}O_3N_3Cl$		0.1503	5.12	12.07	
10	4-Butoxy-2-chlorophenoxyacetone	163	0.2660	8.39	11.19	11.30
	$C_{14}H_{20}O_3N_3Cl$		0.2725	8.58	11.16	
11	2-Ethoxy-4,5-dichlorophenoxyacetone	168-169*	0.1904	17.65	21.70	22.15
	$C_{12}H_{15}O_3N_3Cl$		0.1389	9.05	22.23	
12	2-Butoxy-4,5-dichlorophenoxyacetone	172	0.0507	2.92	20.42	20.36
	$C_{14}H_{19}O_3N_3Cl_2$		0.0426	2.45	20.38	
13	2-Methoxy-4,5-dibromophenoxyacetone	173-174	0.0978	4.99	40.74	40.45
	$C_{11}H_{13}O_3N_3Br_2$		0.1789	9.01	40.25	
14	2-Ethoxy-4,5-dibromophenoxyacetone	176	0.2613	12.70	38.83	39.06
	$C_{12}H_{15}O_3N_3Br_2$		0.1925	9.39	38.97	
15	2-Propoxy-4,5-dibromophenoxyacetone	166.5	0.1156	5.48	37.91	37.77
	$C_{13}H_{17}O_3N_3Br_2$		0.1395	6.61	37.86	
16	2-Butoxy-4,5-dibromophenoxyacetone	172-173	0.1994	9.11	36.51	36.56
	$C_{14}H_{19}O_3N_3Br_2$		0.1934	8.82	36.43	
17	2-Phentyloxy-4,5-dibromophenoxyacetone	171.5	0.1012	4.51	35.63	35.42
	$C_{15}H_{21}O_3N_3Br_2$		0.1718	7.64	35.57	
18	α-Naphthyloxyacetone	196***	0.1683	19.88****	16.54*****	16.33*****
			0.1724	20.02****	16.27*****	
19	2-Benzothiazolylmercaptoacetone [50-53]	182-183	0.1552	22.05****	19.90*****	19.99*****
	$C_{11}H_{12}ON_4S_2$		0.1426	19.97****	19.95*****	

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* Literature: M. p. 180-181° [46].

** Literature: M. p. 196-205 [38].

*** Literature: M. p. 103 [33].

**** Amount of 0.1 N H_2SO_4 required for titration (in ml).

***** Amount of N (in %).

SUMMARY

1. A number of previously unknown aryloxyethanols and aryloxyacetones were synthesized for the purpose of studying their physiological effect on plants.

2. The testing of the indicated compounds as germination inhibitors for radish and flax seed revealed that some of the aryloxyethanols, containing various substituents in the aromatic radical, are strongly inhibitory.

The aryloxyacetones are completely inactive. The activity of the compounds, all containing the same aromatic radicals, decreases in going from the aryloxyacetic acids to the aryloxyethanols, and then to the aryloxyacetones.

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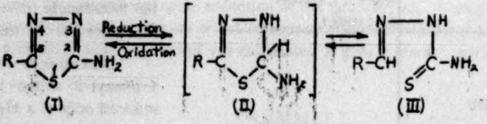
REDUCTION OF THIADIAZOLES WITH RING OPENING

F. F. Medovshchikova and I. Ya. Postovsky

2-Amino-5-alkyl-1,3,4-thiadiazoles (I) are the starting material for the synthesis of bacteriostatic sulfanilamide compounds [1].

It was of interest to obtain the 2,3-dihydro derivatives (II) of these aminothiadiazoles, since such dihydro products appear as though they were cyclic isomers of the thiosemicarbazones (III). As is known, compounds with high antitubercular activity exist among the thiosemicarbazones [2].

The postulation could be made that the dihydro product (II) is also the intermediate substance in the oxidation of the thiosemicarbazones (III) to the 5-alkyl (or aryl)-2-amino-1,3,4-thiadiazoles (I) by the Young method [3].

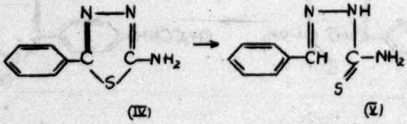


The possibility of obtaining the dihydro product (II) by the careful oxidation of the thiadiazole (I) was not excluded.

If the dihydro product represents an unstable compound, then it should have given the thiosemicarbazone (III) when cleaved.

We subjected to reduction the known compounds: 5-phenyl-2-amino-1,3,4-thiadiazole (IV) [4], 5-p-acetaminophenyl-2-amino-1,3,4-thiadiazole (VI) and 5-methyl-2-amino-1,3,4-thiadiazole (IX). It was revealed that these compounds reduce with difficulty: sodium hydrosulfite in alkaline medium, and also zinc dust in alcohol-alkali medium failed to produce any noticeable changes in the taken thiadiazoles. However, when 5% sodium amalgam in alcohol medium (in the cold) was used as the reducing agent there occurred reduction of the heterocycles containing an aromatic radical in the 5 position, while the thiadiazoles with an aliphatic radical in position 5 failed to be reduced under these reaction conditions.

The reduction of 5-phenyl-2-amino-1,3,4-thiadiazole (IV) gave in 50% yield a product with m. p. 154-155°, identical with the thiosemicarbazone of benzaldehyde; the reduction of 5-p-acetylaminophenyl-2-amino-1,3,4-thiadiazole (VI) gave in the same yield a substance with m. p. 221-222°, proving to be the thiosemicarbazone of p-acetylaminobenzaldehyde.*



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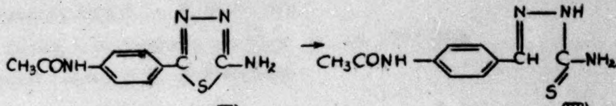
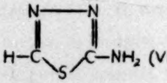
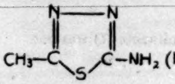
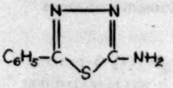
* It is of interest to mention that 5-p-acetylaminophenyl-2-amino-1,3,4-thiadiazole (VI) is without tuberculostatic properties, while the thiosemicarbazone (VII) corresponding to it is a known antitubercular agent.



(VI) (VII)

We assume that the reduction proceeds at the $C^2 - N^3$ bond and that the cyclic dihydro product (II) formed here is cleaved with the formation of the thiosemicarbazone (III), as shown above. It can also be postulated that the reduction fails to proceed at the $C^2 - N^3$, but that under the influence of hydrogen the ring is immediately opened as the result of bond rupture between the C^5 atom and the sulfur atom. However, the latter type of mechanism for explaining the opening of the ring is less probable than the mechanism for opening the ring through the intermediate cyclic dihydro product (II), since the energy of the C – S bond is approximately 24 kcal. greater than for the energy of the π-bond in the group $NH_2-\overset{|}{C}=\overset{|}{N}$.

The difficulty with which the thiadiazoles are reduced, especially those failing to have aromatic radicals in the ring, is also confirmed by the data for the polarographic reduction of certain thiadiazoles, which thiadiazoles are given in the Table.

Thiadiazole	$E_{1/2}$ (V Relative to the Normal Calomel Electrode)
 (VIII)	
 (IX)	
 (IV)	

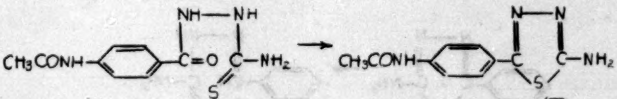
As can be seen from the Table, only the introduction of the aromatic radical into the thiadiazole molecules enables them to be reduced at the mercury dropping electrode.

Attention is drawn to the fact that even 5-phenyl-2-amino-1,3,4-thiadiazole (IV) is reduced only at a high negative half-wave potential, which indicates the difficultly with which the thiadiazole rings are reduced in general.

EXPERIMENTAL

1. Synthesis of Thiadiazoles.- The thiadiazoles used in our work were prepared by methods given in the literature. The thiadiazole (IV) was obtained according to Young by the oxidation of benzaldehyde thiosemicarbazone with ferric chloride under brief boiling [3]. Thiadiazoles (VIII) and (IX) were obtained by the action of acetyl chloride, functioning as a water-removing agent, on the acetyl- and formylthiosemicarbazides, respectively, by the methods described in Freund [5].

The thiadiazole (VI) was obtained by two methods: 1) by the oxidation of p-acetylaminobenzaldehyde thiosemicarbazone with ferric chloride; here satisfactory results are obtained if a solution of ferric chloride is added to a boiling aqueous suspension of the thiosemicarbazone (VII) and the mixture heated for 15 minutes. M. p. 250°, yield 10%; 2) by the ring closure of 1-p-acetylaminobenzoylthiosemicarbazide in the presence of sirupy phosphoric acid as shown in the scheme:



(VI)

Hogarth [6] has described a similar instance of cyclization for other aminothiadiazoles.

Our product had m. p. 250°, and from the analysis data its formula corresponded to that of (VI). The yield was 88%.

Found %: N 23.43. CH_3CO group 1. $C_{10}H_{10}ON_4S$. Calculated %: N 23.85. CH_3CO group 1.

2. Reduction of 5-Phenyl-2-amino-1,3,4-thiadiazole (IV). To a solution of 0.5 g of 5-phenyl-2-amino-1,3,4-thiadiazole (IV) in 40 ml of alcohol was gradually added with mechanical stirring 26 g (10 times the theoretical) of 5% sodium amalgam in small portions over a period of 1 hour. Then the reaction mixture was stirred another 3.5 hours, after which the alcohol solution was decanted from the unreacted amalgam. After dilution with approximately an equal volume of water and removal of most of the alcohol by distillation, the cooled solution was acidified to slightly acid reaction with 2 N hydrochloric acid.

The resulting colorless crystalline precipitate was filtered, washed with water, and dried. Yield 0.25 g (50%). M. p. 155°. Its mixed melting point with benzaldehyde thiosemicarbazone failed to be depressed.

3. Reduction of 5-p-Acetaminophenyl-2-amino-1,3,4-thiadiazole (VI). To a solution of 0.5 g of the thiadiazole (VI) in 50 ml of alcohol was added in the cold over 40-60 minutes 19.6 g (10-fold excess) of 5% sodium amalgam. All further treatment of the reaction mass was the same as described in the preceding experiment.

From the reaction there was obtained 0.25 g of substance with m. p. 222°. Its mixed melting point with p-acetylaminobenzaldehyde thiosemicarbazone failed to be depressed.

With respect to alkalies, acids, and also solvents, the obtained substance behaves the same as p-acetylaminobenzaldehyde thiosemicarbazone.

4. Polarographic Reduction. A visual polarograph of the U.F.A.N. (Ural Affiliate of the Academy of Sciences) system was used for the polarographic reduction of the thiadiazoles. A weighed amount of the substance being studied was dissolved in a known amount of 0.1 M aqueous-alcohol (60% ethyl alcohol) tetramethylammonium iodide solution. The amount of substance taken was calculated to give a solution with a concentration of 10^{-3} mole/liter.

SUMMARY

1. The reduction of the thiadiazoles (IV) and (VI) to the corresponding thiosemicarbazones (V) and (VII) was described, which method represents a new instance for the opening of heterocycles during reduction.

2. It was established that 2-amino-5-methyl-1,3,4-thiadiazole (IX) is a more stable compound than the 5-aryl substituted derivatives (IV) and (VI); it fails to be reduced by 5% sodium amalgam. The greater stability of 5-methyl-2-amino-1,3,4-thiadiazole to reduction when compared with the 5-aryl derivatives of the aminothiadiazoles is also observed during polarographic reduction.

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Ural Polytechnical Institute

Found %: N [illegible] group 1. [illegible] Calculated %: N [illegible] group.

3. Reduction of 5-Phenyl-3-methyl-[illegible] (IV). [illegible] isoxazole (IV) in 30 ml of alcohol was gradually added [illegible] of 3% sodium amalgam in small portions over a period of [illegible]. Then the reaction mixture was stirred [illegible] hours, after which the alcohol solution was decanted from the [illegible] an equal volume of [illegible] was added to [illegible] slightly acid reaction with 50% [illegible].

The resulting colorless crystalline precipitate was filtered, washed with water [illegible] M. p. [illegible] The mixed melting point with [illegible] to be depressed.

4. Reduction of [illegible]. [illegible] of [illegible] diazole (VI) in 50 ml of alcohol was added to the [illegible] of 3% sodium amalgam. All further treatment of the reaction mass was the same as described in the previous experiment.

From the reaction mass there was obtained 0.25 g of substance with m. p. [illegible] or depression.

With respect to alkalies, acids, and the solvents, [illegible] benzoylamino [illegible]

5. Polarographic Reduction. A [illegible] was used for the polarographic [illegible] amount of the substance being studied was dissolved in [illegible] solution. The amount of [illegible] was calculated to give a solution with a concentration of [illegible]

SUMMARY

1. The reduction of [illegible] (IV) and (VI) to the corresponding [illegible] (V) and (VII) was [illegible] method, which [illegible] the opening of [illegible]

2. It was established that [illegible] (IV) and [illegible] it fails to be reduced by sodium amalgam. The greater stability of [illegible] to reduction when compared with [illegible] during polarographic reduction.

LITERATURE CITED

(1) [illegible] "The [illegible] and Allied Compounds" [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

(5) M. Freund [illegible], Ber., [illegible]

(6) [illegible] J. Chem. Soc., [illegible]

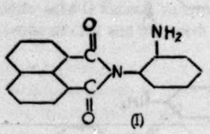
Received May 25, 1954.

[illegible] Pedagogical Institute

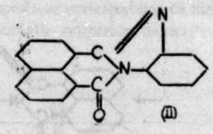
STUDY OF THE PROCESS FOR THE FORMATION OF 1,2-[1',8'-NAPHTHOYLENE] BENZIMIDAZOLE AND ITS AMINOSUBSTITUTED DERIVATIVES

B. M. Krasovitsky and P. M. Matskevich

A method for the preparation of the m- and p-aminophenylimides of naphthalic acid by heating naphthalic anhydride with the nitroanilines in aqueous-alcohol medium in the presence of sodium hydrosulfite has been described by us [1]. Using this method, we wished to obtain under similar conditions the o-aminophenylimide of naphthalic acid; here we obtained two products, of which one (I) proved to be the expected o-aminophenylimide, but in small yield, while the second proved to be identical with the 1,2-[1',8'-naphthoylene] benzimidazole (II), obtained earlier by Bistrzycki [2]:

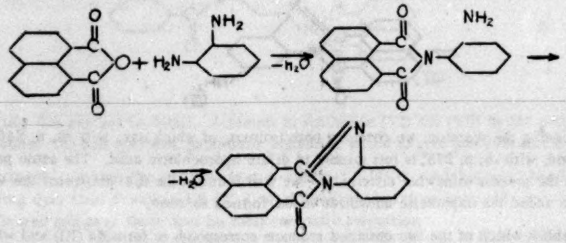


(I)

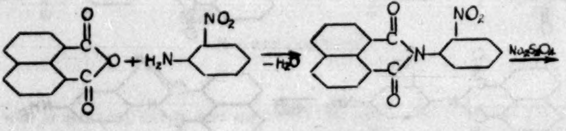


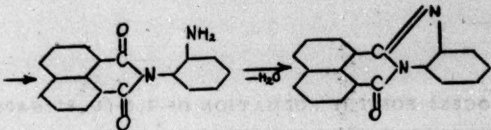
(II)

It could be assumed that the second of these substances is formed in accord with the following scheme: o-nitroaniline is reduced by the hydrosulfite to o-phenylenediamine, which then condenses with naphthalic anhydride to give the o-aminophenylimide of naphthalic acid; the latter, losing one mole of water, is converted into 1,2-[1',8'-naphthoylene] benzimidazole:



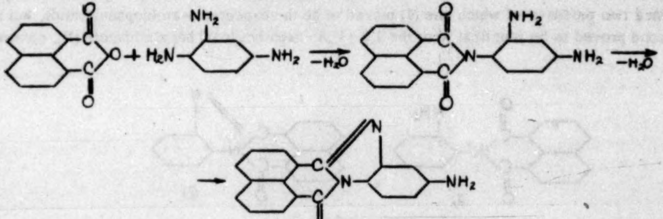
A different scheme for the process is also possible, in accord with which the o-nitrophenylimide is first formed from the naphthalic anhydride and o-nitroaniline, which is then reduced by the sodium hydrosulfite to the aminophenylimide; after one mole of water is cleaved the imidazole ring closes and 1,2-[1',8'-naphthoylene] benzimidazole is formed:



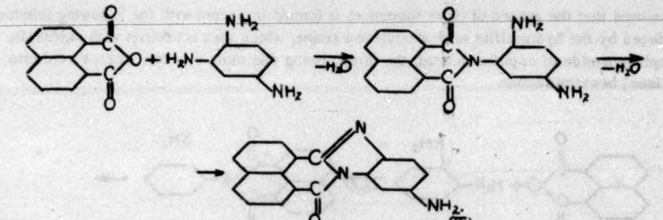


The second of these postulations is the less probable, since naphthalic anhydride in aqueous medium reacts with aniline and its derivatives, containing substituents of the 1st order in the aromatic nucleus, it also reacts with benzidine, but it fails to react with the nitroanilines[3].

If the first scheme is correct and condensation precedes reduction of the nitro compounds, then on heating naphthalic anhydride with 2, 4-dinitroaniline in aqueous-alcohol medium in the presence of sodium hydrosulfite the formation of two isomeric products, both containing the imidazole ring (III and IV), should be expected:



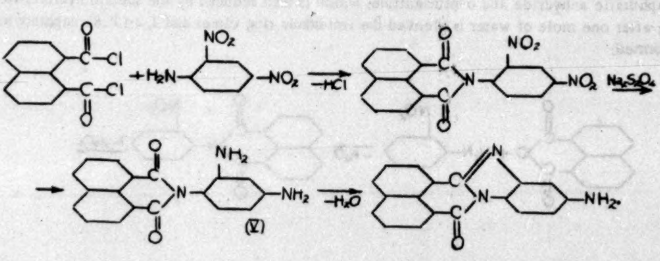
(III)



(IV)

Actually, on running the reaction, we obtained both isomers, of which one, with m. p. 245°, is the more soluble, and the second, with m. p. 275°, is less soluble in dilute hydrochloric acid. The same products were also isolated when we ran the process somewhat differently: we first reduced the 2, 4-dinitroaniline with sodium hydrosulfite, and then added the naphthalic anhydride to the formed solution.

In order to establish which of the two obtained products corresponds to formula (III) and which to formula (IV), we effected the synthesis of compound (III) by the following scheme:

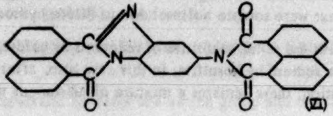


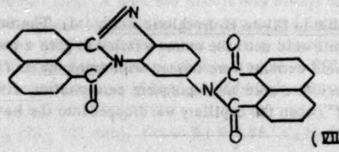
(V)

By condensing the acid chloride of naphthalic acid with 2,4-dinitroaniline under the conditions used by one of us for the preparation of the m- and p-nitrophenylimides of naphthalic acid [4], we obtained the 2,4-dinitrophenylimide of naphthalic acid. Reduction of the latter with sodium hydrosulfite in aqueous-alcohol medium gave 4-amino-1,2-[1',8'-naphthoylene]-benzimidazole (III) in extremely small yield, which compound was identical in all its properties with the amine having m. p. 245°, the compound with the greater solubility in hydrochloric acid. As a result, the less soluble product should have the structure corresponding to formula (IV).

Together with the small yield of the 4-amino-1,2-[1',8'-naphthoylene] benzimidazole obtained in the reduction of the 2,4-dinitrophenylimide of naphthalic acid, the main reaction product, apparently, is the 2,4,-diaminophenylimide of naphthalic acid (V), the isolation of which from its admixture with the sodium hydrosulfite decomposition products, due to its extreme solubility and great ease of air-oxidation, we were unable to achieve; we were able to isolate its dibenzoyl derivative, the analysis of which supported the presence of the diamine itself in the reaction products. As a result, the closure of the imidazole ring in the 2,4-diaminophenylimide molecule, obtained in the reduction of the 2,4-dinitrophenylimide, proceeds with greater difficulty than for the preparation of compounds (III) and (IV) from naphthalic anhydride and 1,2,4-triaminobenzene, the latter being formed in the first stage of the process when naphthalic anhydride is heated with 2,4-dinitroaniline in the presence of sodium hydrosulfite.

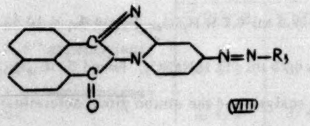
It should be mentioned that together with the formation of compounds (III) and (IV) a product that is insoluble in dilute hydrochloric acid is formed, in its composition corresponding to the compounds that could have been formed in the condensation of (III) and (IV) with naphthalic anhydride, namely (VI) and (VII):

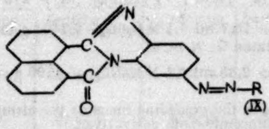

(VI)


(VII)

We did not study this product in detail. Attempts to synthesize (VI) and (VII) by the condensation of the isolated pure compounds (III) and (IV) with naphthalic anhydride failed to give positive results.

It was interesting to compare the azo dyes from 4-amino-1,2-[1',8'-naphthoylene] benzimidazole (VIII) with the corresponding dyes from 5-amino-1,2-[1',8'-naphthoylene] benzimidazole (IX) and to trace the influence of the position of the azo groups in these dyes on their coloristic properties:


(VIII)


(IX)

R— azo component

Dyes (VIII), as well as dyes (IX), fail to show any affinity for cotton (fiber). As acid dyes they dye wool, where the colors show satisfactory resistance to crocking and boiling, but are poor to perspiration.

EXPERIMENTAL*

N-(o-Aminophenyl)naphthalimide and 1,2,-[1',8'-Naphthoylene]-benzimidazole. A mixture of 4.7 g of naphthalic anhydride, 3.6 g of o-nitroaniline and 50 ml of ethyl alcohol in a flask under reflux was brought to the boil on the water bath, after which 25 ml of water was added to the flask and the heating was continued, with small additions (over 30 minutes) of 7.2 g of sodium hydrosulfite. The heating was continued for 2 hours. The obtained precipitate was filtered from the aqueous-alcohol solution and repeatedly treated under heating to 90° with a 10% soda solution to remove unreacted naphthalic acid. When heated with 3% hydrochloric acid a small part of the precipitate goes into solution, from which the o-aminophenylimide of naphthalic acid separates when ammonia is added.

0.1288 g sub.: 8.9 ml 0.1 N H_2SO_4. 0.1516 g sub.: 10.85 ml 0.1 N H_2SO_4. Found %: N 9.67, 10.02. $C_{18}H_{12}O_2N_2$. Calculated %: N 9.72.

N-(o-Aminophenyl)naphthalimide is a pale yellow powder. M. p. 205°. Yield 0.3 g (4%).

The product, insoluble in 3% hydrochloric acid, was recrystallized from glacial acetic acid. After 3 recrystallizations yellow-green crystals with m. p. 187-189° were obtained. Yield 1.5 g (20%) (the 1,2-[1',8'-naphthoylene] benzimidazole obtained by Bistrzycki had m. p. 189°).

4-Amino-1,2,-[1',8'-naphthoylene] benzimidazole and 5-Amino-1,2-[1',8'-naphthoylene] benzimidazole.

a) A mixture of 6.8 g of 2,4-dinitroaniline and 5 g of naphthalic anhydride was suspended in 70 ml of alcohol with heating on the boiling water bath. Then 35 ml of water was added and 28 g of sodium hydrosulfite was sifted in. Heating was continued for 5 hours. The alcohol was distilled off, the precipitate was filtered, and then it was treated with 10% soda solution under heating to remove unreacted naphthalic acid. The reaction product was a mixture of substances that were soluble and insoluble in dilute hydrochloric acid.

b) The condensation was run with the same quantities of reactants as before, but the naphthalic anhydride was added after the introduction of the sodium hydrosulfite; in this case also, after distilling off the alcohol and treating the precipitate with soda solution, there remains a mixture of substances that are soluble and insoluble in dilute hydrochloric acid.

Separation of the Products Soluble in Dilute Hydrochloric Acid. 1) The reaction product was repeatedly treated in the cold with 6% hydrochloric acid until the extracts failed to give a precipitate when ammonia was added. The combined hydrochloric acid extracts were treated with ammonia and the precipitated amine was purified by repeated solution in hydrochloric acid and subsequent precipitation with ammonia. The amine was a brick-red product with m. p. 245-247° (when the capillary was dropped into the bath heated to this temperature). Yield 1.9 g (26.4%).

0.0932 g sub.: 9.6 ml 0.1 N H_2SO_4. 0.1490 g sub.: 15.4 ml 0.1 N H_2SO_4. Found %: N 14.42, 14.50. $C_{18}H_{11}ON_3$. Calculated %: N 14.73.

0.1034 g sub.: 3.75 ml 0.1 N $NaNO_2$. 0.1025 g sub.: 3.70 ml 0.1 N $NaNO_2$.** Found %: $C_{18}H_9ON_2(NH_2)$ 103.6, 103.0.

2) The product, remaining after treatment with cold 6% hydrochloric acid, was heated with the same concentration of acid. The hot hydrochloric acid extract was poured into ammonia; the resulting amine precipitate of yellow-brown color was purified by repeated solution in hydrochloric acid and subsequent precipitation with ammonia. Yield 1.0 g (13.9%). M. p. 275°.

0.1513 g sub.: 15.7 ml 0.1 N H_2SO_4. 0.1301 g sub.: 13.5 ml 0.1 N H_2SO_4. Found %: N 14.53, 14.52. $C_{18}H_{11}ON_3$. Calculated %: N 14.73.

0.1015 g sub.: 3.45 ml 0.1 N $NaNO_2$. 0.1199 g sub.: 4.25 ml 0.1 N $NaNO_2$. Found %: $C_{18}H_9ON_2(NH_2)$ 96.9, 100.9.

Both here and in the preceding instance the nitrogen analysis and the amino group determinations both support the formation of aminoimidazole derivatives.

3) The precipitate, insoluble in 6% hydrochloric acid, was analyzed for nitrogen:

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* Students E. Yu. Rokhlenko and N. I. Titarenko from the Kharkov State University assisted in the experimental portion of this work.

** The course of the diazotization was controlled with the aid of iodide starch paper.

0.1776 g sub.: 11.35 ml 0.1 N H_2SO_4. Found %: N 8.95. $C_{30}H_{15}O_3N_3$. Calculated %: N 9.03.

Thus, the composition of the analyzed substance corresponds to formulas (VI) and (VII). We failed to study this product in greater detail.

N-(2,4-Dinitrophenyl)naphthalimide. The naphthaloyl chloride needed for the work was obtained by the reaction of naphthalic anhydride with phosphorus pentachloride [5]. A mixture of 14 g of naphthaloyl chloride (m. p. 86°) and 11 g of 2,4-dinitroaniline was heated on the water bath for 5 hours in anhydrous benzene. The precipitate was purified by heating with 10% aqueous soda solution, and then with alcohol. Yield 10 g (50%).

The reaction product, a yellow powder with m. p. 210°, is insoluble in water, glacial acetic acid, ethyl alcohol, toluene, xylene and butyl acetate.

0.1553 g sub.: 12.60 ml 0.1 N H_2SO_4. 0.1116 g sub.: 8.95 ml 0.1 N H_2SO_4. Found %: N 11.36, 11.22. $C_{18}H_9O_6N_3$. Calculated %: N 11.57.

Reduction of N-(2,4-Dinitrophenyl)naphthalimide. The N-(2,4-dinitrophenyl)naphthalimide (5 g) was suspended with heating in 50 ml of ethyl alcohol and then 25 ml of water was added. Then, with continued heating on the boiling water bath, 20 g of sodium hydrosulfite was added in small portions over 30 minutes, after which the heating was continued for another 5 hours. After distilling off the alcohol a small amount of the amine deposited, which after two purifications by the method of dissolving in hydrochloric acid and then precipitating with ammonia, melted at 245-246° (when the capillary was dropped into the bath heated to this temperature). The filtrate was evaporated and hydrochloric acid was added to it in the cold. A small amount of precipitate was obtained (apparently, the sulfamino derivative), which dissolved when heated with hydrochloric acid (hydrolysis of the sulfamino derivative) to give the amine as precipitate when ammonia was added, which amine after purification had m. p. 245-246°. Total yield of amine 0.11 g (2.8%).

0.1026 g sub.: 3.65 ml 0.1 N $NaNO_2$. 0.1130 g sub.: 3.9 ml 0.1 N $NaNO_2$. Found %: $C_{18}H_9ON_2(NH_2)$ 101.4, 98.5.

As a result, the obtained substance contains one amino group and is 4-amino-1,2[1',8'-naphthoylene] benzimidazole, identical with product (III). A brownish filtrate was always obtained after isolation of the 4-amino-1,2-[1',8'-naphthoylene] benzimidazole, which filtrate gradually turned dark. By evaporating this filtrate and treating it with benzoyl chloride, by the Schotten-Baumann reaction, we obtained a substance, which after repeated washing with water and recrystallization from aqueous alcohol, had m. p. 207-209°, and which from its nitrogen content corresponded to the dibenzoyl derivative of N-(2,4-diaminophenyl)naphthalimide:

5.920 mg sub.: 0.415 ml N_2 (23°, 737 mm). Found %: N 7.84. $C_{32}H_{21}O_4N_3$. Calculated %: N 8.22.

Dyes from 4-Amino-1,2-[1',8'-naphthoylene] benzimidazole and 5-Amino-1,2-[1',8'-naphthoylene] benzimidazole. A solution of 0.5 g of the amine in 6 ml of 6% hydrochloric acid was diazotized at 0-5° with 0.12 g of sodium nitrite. Sodium acetate was added to the diazo solution to bind the excess hydrochloric acid and then the diazo was coupled with 1-hydroxy-8-aminonaphthalene-3,6-disulfonic acid (0.56 g) and 2-naphthol-3,6-disulfonic acid (0.61 g). The dyes were purified by dissolving in water and then salting them out with sodium acetate, which contamination was then removed by heating the dye with alcohol. The shades, obtained in the dyeing of wool with the dyes obtained from 4-amino-1,2-[1',8'-naphthoylene] benzimidazole, differed but slightly in color and resistance to wet treatments from the dyes obtained from 5-amino-1,2-[1',8'-naphthoylene] benzimidazole. The data on the resistance of the colors to crocking, perspiration and boiling are given in the Table.

Diazo Component	Azo Component					
	1-Hydroxy-8-aminonaphthalene-3,6-disulfonic Acid			2-Naphthol-3,6-disulfonic Acid		
	Crocking	Perspiration	Boiling	Crocking	Perspiration	Boiling
4-Amino-1,2-[1',8'-naphthoylene] benzimidazole	4/4/3	3/4/1	4/4/4	4/4/4	4/4/3	4/4/4
5-Amino-1,2-[1',8'-naphthoylene] benzimidazole	4/4/3	3/4/1	4/4/4	4/4/3	3/4/2	4/4/4

SUMMARY

1. The heating of naphthalic anhydride with o-nitroaniline in aqueous-alcohol medium in the presence of sodium hydrosulfite gave 1,2-[1',8'-naphthoylene] benzimidazole.

2. The heating of naphthalic anhydride with 2,4-dinitroaniline in aqueous-alcohol medium in the presence of sodium hydrosulfite gave 4-amino-1,2[1',8'-naphthoylene] benzimidazole and 5-amino-1,2-[1',8'-naphthoylene] benzimidazole.

3. The azo dyes from the amino derivatives of 1,2-[1',8'-naphthoylene] benzimidazole dye wool in an acid bath; the colors possess satisfactory resistance to crocking and boiling, but show poor resistance to perspiration.

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CYANINE DYES

IX. SOME TETRAMETHOXYTHIACARBOCYANINES

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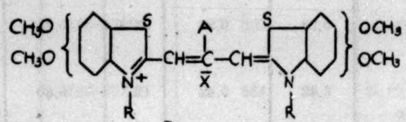
In one of our previous studies it was shown that in the transition from the di- to the tetramethylthiacarbocyanines a noticeable bathochromic shift in the absorption maximum of the dye is observed, in which connection the influence of substituents on the color is additive [1]. It seemed expedient to also study the properties of carbocyanines with two substituents in different positions on the hetero rests, the two substituents possessing a greater polarity and therefore showing a greater influence on the position of the absorption maximum of the dye.

In this connection we synthesized and studied a number of 4,5,4',5'-, 4,6,4',6'-, 4,7,4',7'- and 5,6,5',6'-tetramethoxythiacarbocyanines (I).



(I)

A = H,CH_3 or C_2H_5; R = CH_3 or C_2H_5; X = acidic radical.

Of these dyes a number of the 5,6,5',6'-tetramethoxy derivatives are given in several patents [2] and their use as optical sensitizers for silver halide emulsions is proposed [3]. In these patents it is indicated that the introduction of methoxy groups in the 5,6,5',6'-positions causes a noticeable shift of the absorption maximum in thiacarbocyanines toward the long-wave portion of the spectrum.

TABLE 1

Absorption Maxima of 3,3'-Diethyltetramethoxythiacarbocyanines

Position of the Methoxy Groups	Substituents in the 9 Position		
	H	CH_3	C_2H_5
–	558	543	547
4,5,4',5'	572	550	555
4,6,4',6'	574	562	565
4,7,4',7'	564	548	552
5,6,5',6'	596	575	580

The starting 5,6- and 4,7-dimethoxy-2-methylbenzothiazoles, described earlier by Fries [4, 5], and also the 4,5- and 4,6-dimethoxy derivatives, were obtained by us by the oxidation of the thioacetyl derivatives of the corresponding aminodimethoxybenzenes with potassium ferricyanide (cf. [6]).

The oxidation of 4-thioacetamino-1,3-dimethoxybenzene yielded appreciable amounts of the corresponding disulfide, which we were able to isolate in the pure state.

The dyes were synthesized by heating the reacting alkyl-p-toluenesulfonates of the dimethoxy-2-methylbenzothiazoles with the ortho esters of carboxylic acids in pyridine (cf. [7]) and were isolated as well-crystallized iodides.

The absorption maxima of the obtained 3,3'-diethyltetramethoxythiacarbocyanines (in ethyl alcohol) are given in Table 1.

TABLE 2

Name of dyes	Amount of free base (in g)	Amount of p-toluene-sulfonic acid ester (in g)	Ortho ester*	Amount of ortho ester (in g)	Amount of pyridine (in ml)	Yield (in % of the theoretical)
3,3'-Diethyl-4,5,4',5'-tetramethoxythiacarbocyanine Iodide	0.21	0.21	OE1	0.30	2.0	75
3,3'-Diethyl-9-methyl-4,5,4',5'-tetramethoxythiacarbocyanine Iodide	0.21	0.21	OE2	0.33	2.0	38
3,3',9-Triethyl-4,5,4',5'-tetramethoxythiacarbocyanine Iodide	0.21	0.21	OE3	0.36	2.0	31
3,3'-Dimethyl-9-ethyl-4,5,4',5'-tetramethoxythiacarbocyanine Iodide	0.21	0.20	OE3	0.36	2.0	62
3,3'-Diethyl-4,6,4',6'-tetramethoxythiacarbocyanine Iodide	0.21	0.21	OE1	0.30	1.0	55
3,3'-Diethyl-9-methyl-4,6,4',6'-tetramethoxythiacarbocyanine Iodide	0.21	0.21	OE2	0.32	1.0**	33
3,3',9-Triethyl-4,6,4',6'-tetramethoxythiacarbocyanine Iodide	0.21	0.21	OE3	0.26	1.0**	42
3,3'-Dimethyl-9-ethyl-4,6,4',6'-tetramethoxythiacarbocyanine Chloride	0.21	0.20	OE3	0.26	1.0**	38
3,3'-Diethyl-4,7,4',7'-tetramethoxythiacarbocyanine Iodide	0.42	0.42	OE1	0.60	2.5	75
3,3'-Diethyl-9-methyl-4,7,4',7'-tetramethoxythiacarbocyanine Iodide	0.42	0.42	OE2	0.64	2.5	35
3,3',9-Triethyl-4,7,4',7'-tetramethoxythiacarbocyanine Iodide	0.42	0.42	OE3	0.70	3.0	23.5
3,3'-Dimethyl-9-ethyl-4,7,4',7'-tetramethoxythiacarbocyanine Iodide	0.42	0.40	OE3	0.70	3.0	34
3,3'-Diethyl-5,6,5',6'-tetramethoxythiacarbocyanine Iodide	0.42	0.42	OE1	0.60	2.5	78
3,3'-Diethyl-9-methyl-5,6,5',6'-tetramethoxythiacarbocyanine Iodide	0.42	0.42	OE2	0.64	3.0	46
3,3',9-Triethyl-5,6,5',6'-tetramethoxythiacarbocyanine Iodide	0.42	0.42	OE3	0.70	3.0	34
3,3'-Dimethyl-9-ethyl-5,6,5',6'-tetramethoxythiacarbocyanine Iodide	0.42	0.40	OE3	0.70	3.0	30

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* OE1 — ethyl orthoformate, OE2 — ethyl orthoacetate, OE3 — ethyl orthopropionate.

** 0.10 g of acetic anhydride was added.

*** The amount of N is given.

These data, part of which were briefly published by us earlier [9], show that the transition from the di- [8] to the tetramethoxythiacarbocyanines in the case of the 4,6,4',6'-, 4,7,4',7'- and 5,6,5',6'-derivatives results in deepening of the color, while at the same time the absorption maximum for the 4,5,4',5'-tetramethoxy derivatives lies between the absorption maxima for the 4,4'- and 5,5'-dimethoxythiacarbocyanines.

It should be mentioned that the bathochromic effect produced as the result of introducing methoxy groups in the 5,6,5',6'-positions of these dyes is somewhat greater than the sum of the shifts produced by the substituents in the corresponding dimethoxythiacarbocyanines (38 mμ versus 32 mμ).

External appearance	Melting point	Absorption maximum in mμ (in C_2H_5OH)	Analysis		
			Found	Calculated	
			I (%)	Formula	I (%)
Red needles with greenish case	223-224°	572	20.85	$C_{25}H_{29}O_4N_2S_2I$	20.73
Dark-green prisms	215-217	550	20.39	$C_{26}H_{31}O_4N_2S_2I$	20.27
Dark-green prisms	202-203	555	20.01	$C_{27}H_{33}O_4N_2S_2I$	19.82
Red prisms	206-208	552	20.89	$C_{25}H_{29}O_4N_2S_2I$	20.73
Purple prisms	248-250	574	4.64•••	$C_{25}H_{29}O_4N_2S_2I$	4.57•••
Bluish-purple prisms	224-225	562	4.52•••	$C_{26}H_{31}O_4N_2S_2I$	4.47•••
Brown prisms with greenish cast	222-223	565	4.46•••	$C_{27}H_{33}O_4N_2S_2I$	4.37•••
Lustrous brown prisms with greenish cast	174-176	562	5.49•••	$C_{25}H_{29}O_4N_2S_2Cl$	5.37•••
Bluish-purple needles	224-225	564	20.88	$C_{25}H_{29}O_4N_2S_2I$	20.73
Brownish-red crystals	206-207	548	20.39	$C_{26}H_{31}O_4N_2S_2I$	20.27
Green leaflets with golden luster	210-212	552	19.68	$C_{27}H_{33}O_4N_2S_2I$	19.82
Reddish-purple needles	210-211	550	20.62	$C_{25}H_{29}O_4N_2S_2I$	20.73
Green prisms	249-250	596	20.86	$C_{25}H_{29}O_4N_2S_2I$	20.73
Bluish-purple prisms	241-242	575	20.42	$C_{26}H_{31}O_4N_2S_2I$	20.27
Blue needles with a steel luster	222-223	580	19.93	$C_{27}H_{33}O_4N_2S_2I$	19.82
Brownish-red prisms	236-237	576	20.82	$C_{25}H_{29}O_4N_2S_2I$	20.73

The abnormally heightened color of the 4,5,4',5'-tetramethoxythiacarbocyanines can possibly be associated with stearic difficulties involved in the electron reaction of the methoxy groups with the polymethine chromophore (cf. [10, 11]).

The space models of these dyes, constructed with the interatomic distances and valence angles taken into consideration, show that in them the methoxy groups and the hydrocarbon radical on the nitrogen atom cannot lie in the same plane. In association with this in the 4,5,4',5'-tetramethoxythiacarbocyanines the electron shifts from the methoxy groups are apparently weakened, which should lead to a heightening of the color (cf. [10-13]).

The investigated tetramethoxythiacarbocyanines are average in their properties as optical sensitizers. The least sensitizing ability is possessed by the 4,7,4',7'-derivatives, which, possibly, is associated with the presence of substituents in the 7,7'-positions (cf. [8]). The ability of the investigated tetramethoxythiacarbocyanines for 2nd order sensitization is quite weakly expressed [14].

EXPERIMENTAL

(Jointly with Z. Ya. Bukshpan)

3-Acetaminoveratrole. Obtained by a slight modification of the Vermeulen method [15]. A mixture of 4.6 g of freshly distilled 3-aminoveratrole and 6.4 ml of acetic anhydride was allowed to stand; the next day the reaction mixture was diluted with 40 ml of water, cautiously neutralized with soda, the product filtered, washed with water, and dried. Yield 5.4 g (95%). M. p. 82-83° (according to Vermeulen [15], m. p. 84°). Colorless prisms (from dilute alcohol).

To obtain the starting 3-aminoveratrole, m-nitroanisole was nitrated with nitric acid (d 1.5) to give the 2,3-dinitroanisole [16], which with sodium methylate [17] was converted into 3-nitroveratrole. The latter was then reduced with iron in weakly acid medium [18].

3-Thioacetamino-1,2-dimethoxybenzene. To a solution of 1.95 g of 3-acetaminoveratrole in 20 ml of boiling dry benzene was gradually added 0.56 g of finely ground phosphorus pentasulfide. Then the mixture was boiled under reflux for 25 minutes, the benzene solution was decanted from the tarry deposit and the latter was washed with 20 ml of benzene, which was added to the main solution. The benzene solution was shaken with 80 ml of 5% sodium hydroxide solution [in 4 portions (doses)]. The alkaline solution was neutralized with acetic acid, and the thioacetyl derivative was isolated by the passage of carbon dioxide gas. The pale yellow precipitate was filtered, washed with water, and dried. Yield 0.72 g (34%). M. p. 76-78°. For analysis the product was recrystallized from ethyl alcohol. Almost colorless needles, M. p. 81°.

Found %: N 6.58, 6.71. $C_{10}H_{13}O_2NS$. Calculated %: N 6.63.

4-Thioacetamino-1,3-dimethoxybenzene. Obtained in the same manner as the previous compound from 19.5 g of 4-acetamino-1,3-dimethoxybenzene (m. p. 114-115° [19]) by heating with 11.0 g of phosphorus pentasulfide in 300 ml of dry benzene for 2 hours. The thioacetyl derivative was extracted from the benzene solution by shaking with a 2% sodium hydroxide solution (10 times with 200 ml portions). Yield 51%. M. p. 88-89°. Pale yellow lustrous prisms (from ethyl alcohol, 1: 5). M. p. 89-90°.

Found %: N 6.81. $C_{10}H_{13}O_2NS$. Calculated %: N 6.63.

2-Methyl-4,5-dimethoxybenzothiazole. A solution of 4.2 g of 3-thioacetaminoveratrole in 42 ml of 8% potassium hydroxide solution at 0-5° was gradually added with stirring to a solution of 13.2 g of potassium ferricyanide in 65 ml of water. The next day the liquid was extracted with ether, the extract dried over potash, the ether distilled off, and the residue (3.2 g) converted to the picrate in alcohol solution (3.7 g of picric acid in 10 ml of alcohol). The insoluble picrate was filtered and thoroughly washed with ether. Yield 5.4 g (61%). Decomposition of the picrate with aqueous soda solution gave 2.25 g of the free base as yellowish crystals with m. p. 56-58°. For purification the latter were recrystallized twice from gasoline. Colorless prisms with m. p. 61.5-62°. Readily soluble in alcohol and benzene, and quite difficultly soluble in cold ligroine.

Found %: N 6.79. $C_{10}H_{11}O_2NS$. Calculated %: N 6.70.

Picrate — yellow prisms (from ethyl alcohol). M. p. 129-130°.

Found %: N 12.87. $C_{16}H_{14}O_9N_4S$. Calculated %: N 12.78.

2-Methyl-4,6-dimethoxybenzothiazole. A filtered solution of 4.22 g of 4-thioacetamino-1,3-dimethoxybenzene and 2.4 g of sodium hydroxide in 60 ml of 30% ethyl alcohol was added with stirring over 30 minutes at 0-5° to a solution of 13.2 g of potassium ferricyanide in 90 ml of water. The next day the obtained precipitate was extracted with ether, and the ether extracted was repeatedly shaken with 10% hydrochloric acid (4 times with 50 ml portions). The acid water solution was made alkaline to give the free base as a nearly colorless precipitate. Yield 1.30 g (31%). M. p. 53-55°.

Colorless prisms (from gasoline with b. p. 60-70°). M. p. 58-59°. Very easily soluble in alcohol, ether and benzene, and somewhat less soluble in gasoline.

Found %: N 6.71. $C_{10}H_{11}O_2NS$. Calculated %: N 6.69.

Picrate – pale yellow prisms (from alcohol, 1 : 30). M. p. 173-174°.

The ether solution after extracting the free base was washed with 2% sodium hydroxide solution and water, dried over sodium sulfate, and the ether distilled off to leave a brown residue that completely crystallized on cooling. Weight 1.81 g (43%). M. p. 74-76°. Colorless needles (from ethyl alcohol, 1 : 4). M. p. 84-85°. Insoluble in aqueous alkalies and acids at room temperature. Readily soluble in alcohol and benzene.

Found %: N 6.55, 6.50. $C_{20}H_{24}O_4N_2S_2$. Calculated %: N 6.66.

Sulfur and hydrogen sulfide were liberated when 0.5 g of the substance was boiled for 30 minutes with 5 ml of 20% hydrochloric acid. A nearly colorless precipitate was obtained when 0.6 g of acetic anhydride was added to the soda-neutralized solution, which after recrystallization from dilute alcohol had m. p. 114-115°, and which failed to show a melting point depression when mixed with 4-acetamino-1,3-dimethoxybenzene.

2-Methyl-4,7-dimethoxybenzothiazole. Synthesized in the same manner as the preceding compound from 2-thioacetamino-1,4-dimethoxybenzene, with purification through the picrate. Yield 75%. Colorless needles (from ethyl alcohol). M. p. 100-101° (Fries [5] gives m. p. 101°).

Picrate – yellow needles (from ethyl alcohol). M. p. 155-156°.

Methiodide. A mixture of 0.42 g of 2-methyl-4,7-dimethoxybenzothiazole and 0.28 g of methyl iodide was heated for 5 hours on the boiling water bath in a flask under reflux; then 0.14 g of methyl iodide was added, and the heating was continued for another 5 hours. The crystalline mass was washed with benzene and boiling acetone. Yield 81%. Slightly grayish prisms (from anhydrous ethyl alcohol). M. p. 209-210°.

Found %: I 36.24. $C_{11}H_{14}O_2NSI$. Calculated %: I 36.15.

The Ethiodide was obtained in the same manner as the preceding compound; the duration of heating was increased to 20 hours. Yield 88%. Grayish needles (from ethyl alcohol . M. p. 221-222°.

Found %: N 3.92, 3.95. $C_{12}H_{16}O_2NSI$. Calculated %: N 3.84.

The Propiodide was obtained by heating 2-methyl-4,7-dimethoxybenzothiazole with a 20% excess of propyl iodide at 110-120° for 15 hours. Yield 63%. Slightly greenish needles (from anhydrous ethyl alcohol). M. p. 186-187°.

Found %: I 33.56, 33.62. $C_{13}H_{18}O_2NSI$. Calculated %: I 33.48.

The Methyl-p-toluenesulfonate – nearly colorless find needles (from acetone). M. p. 149-150°.

Found %: S 16.35. $C_{18}H_{21}O_5NS_2$. Calculated %: S 16.22.

2-Methyl-5,6-dimethoxybenzothiazole. Obtained by the Fries method [4] of oxidizing 4-thioacetaminoveratrole with potassium ferricyanide. Colorless crystals (from ethyl alcohol). M. p. 75-76° (literature m. p. 75°[4]).

Picrate – yellow prisms (from ethyl alcohol, 1 : 100). M. p. 204-205°.

Tetramethoxythiacarbocyanines. To obtain the 3,3'-diethyltetramethoxythiacarbocyanines the dimethoxy-2-methylbenzothiazoles were heated with a 5% excess of ethyl p-toluenesulfonate at 140-145° for 6 hours. In the synthesis of the 3,3'-dimethyl derivatives the methyl-p-toluenesulfonates were obtained in similar manner, in in which connection the heating was done at 130-135°. Pyridine and the ortho ester of the carboxylic acid were added to the obtained quaternary salt, and the mixture was heated in an oil bath at 130-135° for 1 hour. Then the reaction mass was diluted with ether, the tarry precipitate dissolved in methyl alcohol, and the dye iodide isolated by the addition of aqueous potassium iodide solution. For purification the dyes were well washed with water and alcohol, after which they were recrystallized from ethyl alcohol until the melting point remained constant. Prior to analysis the dyes were dried *in vacuo* at 70-100° to constant weight.

The preparation conditions and yields of the dyes, their properties, and the analysis results, are all given in Table 2.

The absorption curves of the dyes were measured on a Koenig-Martens spectrophotometer in $1 \cdot 10^{-4}$ molar ethyl alcohol solutions.

SUMMARY

1. The 4,5- and 4,6-dimethoxy-2-methylbenzothiazoles were synthesized. From the quarternary salts of these compounds, and also from the earlier described 4,7- and 5,6-derivatives, were obtained a number of

4,5,4',5'-, 4,6,4',6'-, 4,7,4',7'- and 5,6,5',6'-tetramethoxythiacarbocyanines. The optical and photographic properties of these dyes were studied.

2. It was shown that in the transition from the dimethoxy- to the tetramethoxythiacarbocyanines a deepening of the color is observed for the 4,6,4',6'- 4,7,4',7'- and 5,6,5',6'-derivatives, while at the same time the absorption maximum for the 4,5,4',5'-tetramethoxy derivatives lies between the absorption maxima of the 4,4'- and 5,5'-dimethoxythiacarbocyanines.

3. The postulation was expressed that the heightened color of the 4,5,4',5'-tetramethoxythiacarbocyanines was associated with hindered electron reaction of the methoxy groups in these dyes with the polymethine chromophore due to spatial difficulties.

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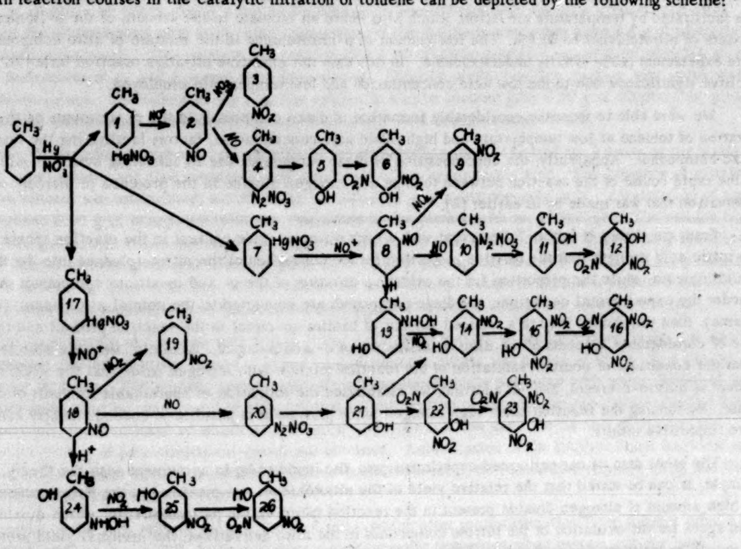
MECHANISM FOR THE CATALYTIC NITRATION OF AROMATIC COMPOUNDS IN THE PRESENCE OF MERCURY SALTS

III. NEW DIRECTIONS FOR THE REACTION IN THE NITRATION OF TOLUENE

A. I. Titov and A. N. Baryshnikova

The nitration of toluene with nitric acid in the presence of mercury was studied by Davis and coworkers [1], and also by Blechta and Patek [2]. From the nitration products they were able to isolate the nitrotoluenes, p-nitrobenzoic acid and trinitro-m-cresol. The main purpose of the present study was to show the application of our earlier developed theory [3] to finding new chemical phenomena in this reaction.

The main reaction courses in the catalytic nitration of toluene can be depicted by the following scheme:



The primary reaction products are the p-, o- and m-tolylmercury nitrates 1, 7 and 17, which under the influence of nitrogen dioxide are farther converted into the nitroso compounds 2, 8 and 18. The nitrosotoluene 2, as well as all of the nitroso compounds having substituents in the p-position to the nitroso group, under the influence of nitrogen dioxide are converted into p-nitrotoluene 3, while in the reaction with nitrogen oxide they are converted into p-toluenediazonium nitrate 4, which can be easily converted into p-cresol and then into dinitro-p-cresol 6.

The o-nitrosotoluene 8 and its m-isomer 18, originating in the same manner as the p-isomer, in addition to the indicated transformations into nitrotoluenes 9 and 19, diazo compounds 10 and 20 and normal nitrophenols 12 and 23, are also capable, under hydrogen-ion influence, of transition into the p-hydroxyhydroxylamines 13 and 24, which under the reaction conditions, in the final analysis, are converted into the anomalous nitrophenols 15, 16 and 26. The anomalous nitrophenols, in contrast to the normal analogs, have the hydroxyl group in the para-positions to the site occupied earlier by the nitroso group and mercury atom. We termed the simultaneous introduction of the nitro and hydroxyl groups as oxidative nitration [3].

The possibility and degree of conversion of the nitroso compounds by one or the other path depends on their structure, concentration of components in the equilibrium system $2HNO_3 + NO \rightleftharpoons 3NO_2 + H_2O$, and the temperature. In accord with earlier statements, the p-nitrosotoluene is practically incapable of conversion into the anomalous nitrophenols. The entrance of the o- and m-nitrosotoluenes into the oxidative nitration reaction is favored by an increase in acid concentration and by elevation of the temperature. It is natural for an increase in the nitrogen oxide concentration to facilitate the conversion of all of the nitrosotoluenes into diazo compounds, which are easily transformed at slightly elevated temperatures into the normal nitrophenols. A high nitrogen dioxide concentration should assure oxidation of the nitrosotoluenes to the nitrotoluenes.

The results for the experimental verification of the theoretical conclusions are given below.

With the oxidative nitration reaction representing a fairly high proportion of the total sum of the reactions, with only the o- and m-nitrosotoluenes entering into it, then in the mixture of formed nitrotoluenes the p-isomer should predominate. The validity of such a conclusion is well supported by our experimental data (cf. Experimental). In the first experiment a comparatively high nitric acid concentration facilitated oxidative nitration, and the amount of the p-isomer in the mixture of nitrotoluenes reached 62%, while in the usual mixture it is only 40%. In the second experiment the conversion of the o- and m-nitrosotoluenes into the anomalous nitrophenols was facilitated by temperature elevation, which also led to an increase in the amount of the p-isomer in the mixture of nitrotoluenes to 60.6%. The low amount of p-nitrotoluene in the mixture of nitro compounds from the third experiment (43%) is fully understandable. In this case the oxidative nitration reaction failed to possess decisive significance due to the low acid concentration and low temperature employed.

We were able to show the considerable formation of diazo compounds in the experiments on the catalytic nitration of toluene at low temperature and high nitric acid concentration, factors facilitating the retention of diazo compounds. Apparently, the decomposition of diazo compounds and its initiating action should be explained by the rapid course of the reaction between toluene and nitrogen dioxide in the presence of mercury nitrate, an observation that was made by us earlier [5].

From our theory it further follows that with a high nitrogen oxide content in the reaction sphere and with a low nitric acid strength that the relative proportion for the conversion of the nitrosotoluenes into the diazo compounds should increase, while the proportion for the oxidative nitration of the o- and m-nitroso compounds should decrease. If, under the experimental conditions, the diazo compounds are converted to the normal nitrophenols (cf. main scheme), then this should lead to a reduced amount of trinitro-m-cresol in the reaction product and to the appearance of considerable amounts of the dinitro derivatives of o- and p-cresol. Actually, we were able to show that under the conditions of constant saturation of the reaction mixture with nitrogen oxide that the main reaction product is dinitro-o-cresol, and, in addition, we established the formation of appreciable amounts of dinitro-p-cresol. By running the reaction under high nitrogen oxide pressure it is possible to unconditionally achieve even more impressive results.

The other data of our performed experiments are also found to be in agreement with the theory. Thus, for example, it can be stated that the relative yield of the nitrotoluenes was maximal in the first experiment due to the high amount of nitrogen dioxide present in the reaction sphere in the particular case, which dioxide functioned as an agent for the oxidation of the nitroso compounds to the nitro derivatives; the minimal yield proved to be in the second experiment due to shifting of the equilibrium $NO_2 + NO \rightleftharpoons N_2O_3$ to the right and suppression of the reaction for the oxidation of the nitrosotoluenes to the nitro derivatives due to transformation of the first to diazo compounds and their decomposition products.

The diversity of the chemical reactions in the catalytic nitration of toluene is far from being limited to the earlier examined directions. For example, the possibility should be mentioned of converting the nitrosotoluenes into the o- and p-dinitro derivatives, the nitrosoditolylhydroxylamines, etc. [3, 4]. It is also important to mention that due to the presence of nitrogen dioxide in the reaction sphere the paraffinic (alkyl) chain of toluene is drawn into reaction [6]. Thus, in the first experiment we were able to show the formation, besides p-nitrobenzoic acid, of benzyl nitrate and p-nitrobenzoate. In accord with our investigations [7], the source for the creation of p-nitrobenzoic acid is phenyldinitromethane, reacting in accord with the scheme:

$$C_6H_5CH(NO_2)_2 \xrightarrow{NO_2} C_6H_5C(NO_2)_3 \rightarrow p\text{-}NO_2C_6H_4-COOH,$$

while the formation of the phenylnitromethane and of benzyl alcohol and its esters was examined earlier [6].

To demonstrate the presence of benzyl p-nitrobenzoate in the reaction product we made use of its reaction with diethylamine, $p\text{-}NO_2-C_6H_4-COO-CH_2-C_6H_5 + NH(C_2H_5)_2 \rightarrow p\text{-}NO_2-C_6H_4-COOH + C_6H_5-CH_2-N(C_2H_5)_2$, to yield the free p-nitrobenzoic acid and benzyldiethylamine. The alkylation influence manifested by the ester, instead of an acylation action, as was determined (shown) by us earlier [8], is closely associated with the ease with which the benzyl group is converted into the benzyl cation and with the diminished electrophilic activity of the carboxylic carbon atom in acids of type Ar − COOH due to conjugation with the π-electrons of the nucleus.

EXPERIMENTAL

1. Oxidative Nitration of Toluene with Concentrated Nitric Acid at Around 5 to 10°. A mixture of 40 ml of toluene, 100 ml of nitric acid (d 1.32), 10 g of mercury nitrate and 2 g of sodium nitrate was allowed to stand in a one liter conical flask fitted with a ground-glass calcium chloride tube, filled with anhydrous calcium nitrate. After 10 days the acid layer was fortified with 40 ml of nitric acid (d 1.5) and 10 g of the mercury salt.

After 25 days of standing the reaction mass was cooled to 0°, filtered, and washed with 30 ml of cold toluene. From the precipitate 1.3 g of p-nitrobenzoic acid with m. p. 220-225° was isolated. Titration of the acid layer with β-naphthol showed the presence of about 1.3 g of mixed isomeric toluenediazonium nitrates. The organic layer was successively extracted with water, soda and alkali solutions, and then dried over potash. The soda extract was acidified, and the separated oil was steamdistilled. The residue in the distillation flask gave 1.84 g of trinitro-m-cresol with m. p. of about 90-100°, giving a higher melting point when heated with the pure product, and after recrystallization the trinitrocresol with m. p. 105°. Extraction of the distillate with ether gave 2.4 g of partially crystallized mixed nitrocresols. This mixture was treated with 1 ml of nitric acid (d 1.4) and 3 ml of H_2SO_4 at 100°; here the nitro derivatives of o- and p-cresol were decomposed. Dilution of this reaction mixture with water yielded 1.3 g of trinitro-m-cresol. Treatment of the alkaline extract in similar manner gave 0.52 g of nitrocresols, yielding 0.24 g of trinitro-m-cresol when treated with sulfuric acid-nitric acid mixture (mixed acid).

The toluene layer after drying was mixed with 10 ml of diethylamine and heated for 4 hours on the water bath in a flask under reflux, and then extracted with water and dilute hydrochloric acid. The presence of nitrate ion in the water extract was established; acidification yielded 0.12 g of p-nitrobenzoic acid. Alkalization of the acid extract yielded 0.31 g of benzyldiethylamine, identified as the picrate with m. p. 122° [8]. The residue from the preceding treatments was steam-distilled, the organic layer of the distillate dried, and then vacuum-distilled to yield 10.2 g of mixed nitrotoluenes with freezing point 25.5°, which corresponds to a 62% content of the p-isomer compared with 40% in the usual mixture. Without doubt the amount of p-isomer in the nitro product from this experiment was somewhat reduced due to the occurrence of parallel nitration through the nitronium cation.

2. Oxidative Nitration of Toluene with Dilute Nitric Acid Under Saturation with Nitrogen Oxide. A mixture of 50 ml of toluene, 200 ml of nitric acid (d 1.1) and 40 g of mercury nitrate was heated at 50-60° in a current of nitrogen oxide for 50 hours. The organic portion with stirring was successively extracted with water, 20 ml of 10% potassium bicarbonate solution, and 20 ml of soda solution. Acidification of the bicarbonate extract yielded 3.3 g of mixed nitrocresols, the treatment of which with 20 ml of 10% soda solution gave the Na salt of trinitro-m-cresol, from which 0.73 g of pure trinitro-m-cresol was obtained. Acidification of the mother liquor from the salts yielded 2.4 g of oil; its steam-distillate yielded dinitro-o-cresol with m. p. 83°, while the residual oil in the flask yielded 0.93 g of crystalline trinitro-m-cresol.

Acidification of the soda extract yielded 2.5 g of solid, which after recrystallization from alcohol gave 1.3 g of dinitro-o-cresol with m. p. ca. 83°, failing to show a melting point depression when mixed with the pure authentic product. Treatment of the alcohol mother liquor with 20 ml of 10% potash solution yielded 0.5 g of mixed potassium salts of the dinitro derivatives of o- and p-cresol. Recrystallization of the mixture from water gave 0.12 g of the bright red salt of dinitro-p-cresol, from which dinitro-p-cresol with m. p. 80-82° was isolated, failing to show a melting point depression when mixed with pure 2,6-dinitro-4-methylphenol. From the residue after the extraction with carbonate solutions the usual operations of drying and vacuum-distillation yielded 1.4 g of mixed nitrotoluenes with a freezing point of 7°.

3. Oxidative Nitration of Toluene with Dilute Nitric Acid at 100° Without Nitrogen Oxide Saturation. A mixture of 20 ml of toluene, 100 ml of nitric acid (d 1.1), 20 g of mercury nitrate and 0.2 g of trioxymethylene was heated for 10 hours on the boiling water bath in a flask under reflux. Treatment of the reaction mixture in the same manner as just described yielded 2.19 g of trinitro-m-cresol, 0.15 g of dinitro-o-cresol, 0.8 g of mixed nitrocresols, 2.3 g of mixed nitrotoluenes with freezing point 24.5°, and 7.6 g of insoluble mercury salts and polyorganomercury compounds.

4. Alkylation with the Benzyl Esters of Benzoid and p-Nitrobenzoid Acid. A mixture of 1 g of benzyl p-nitrobenzoate, 5 ml of nitrobenzene and 3 ml of diethylamine was heated for 8 hours on the water bath in a small flask under reflux, after which it was successively treated with water and dilute hydrochloric acid, and then steam-distilled. The water extract yielded 0.12 g of p-nitrobenzoic acid. Treatment of the acid extract in the usual manner yielded 0.15 g of benzyldiethylamine, identified as the picrate and from its mixed melting point with the authentic product. The residue from the steam-distillation yielded 0.73 g of the p-nitrobenzoate with m. p. around 80°. We were able to show that alkylation also took place in a similar experiment with benzyl benzoate.

SUMMARY

1. In accord with the theory for the reaction it was found that in the catalytic nitration of toluene the following holds:

a) the mixture of nitrotoluenes can have a high content of the para-isomer;

b) toluenediazonium salts are formed;

c) when dilute nitric acid is used and the reaction mixture is saturated with nitrogen oxide, the main reaction product is dinitro-o-cresol with the concurrent formation of the nitro derivatives of m- and p-cresol;

d) the yield of nitrotoluenes is increased with increase in the nitrogen dioxide concentration.

2. The presence of benzyl p-nitrobenzoate and benzyl nitrate in the reaction product was shown and the mechanisms for their formation were indicated.

3. The benzyl esters of the aromatic acids of type Ar – COOH function as alkylation agents in the reaction with diethylamine.

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ACTION OF ALKYL IODIDES ON ESTERS OF PHENYLALKYLARSENIOUS ACIDS

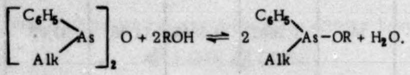
I. M. Starshov and Gilm Kamai

In previous communications one of us [1, 2] had shown that the esters of the arsenious acids: $As(OR)_3$, $ArAs(OR)_2$ and Ar_2AsOR, in constrast to the analogous esters of phosphorous and the arylphosphinic acids, under the influence of alkyl halides in the conditions of the Arbuzov rearrangement [3], fail to be isomerized into pentavalent arsenic compounds. It was also established that the cuprous halides react to form crystalline addition products with only those esters of arsenious acid as more closely resemble the arsines in their properties.

The mixed cyclic esters of arsenious acid also fail to react with alkyl iodides and with cuprous halides [4].

In the present communication we describe the results obtained when we studied the reaction of cuprous chloride and of alkyl halides with a number of phenylalkylarsenious acid esters.

Our starting substances were the alkyl iodides (where R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9) and the esters that were obtained in the reaction of the corresponding alcohols with bis(phenylalkylarsine) oxides in accord with the equation:



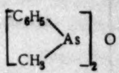
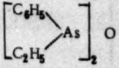
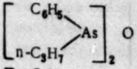
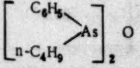
$$\left[(C_6H_5)(Alk)As\right]_2O + 2ROH \rightleftharpoons 2\,(C_6H_5)(Alk)As{-}OR + H_2O.$$

The reaction of alcohols with the oxides of secondary aralkyl arsines under conditions approximating those used for the esterification of arsenious anhydride [5] and phenylarsine oxide (arsenosobenzene) [6] with alcohols was realized for the first time in this study.

In this way we prepared the methyl, ethyl, n-propyl and n-butyl esters of phenylmethyl-, phenylethyl-, phenyl-n-propyl- and phenyl-n-butylarsenious acids. These esters, as derivatives of trivalent arsenic, lie close to the arsines in their properties, and easily add the cuprous halides, as well as the alkyl bromides and iodides.

The alkyl iodide addition products of the esters – the phenyldialkylalkoxyarsonium iodides – are colorless crystalline substances.

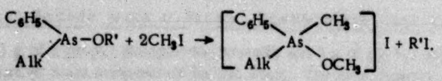
TABLE 1

Formula	Boiling point	d_0^{20}	n_D^{20}	MR	AR_{As}	% As		Yield (in %)
				Found	Found	Found	Calculated	
 $\left[(C_6H_5)(CH_3)As\right]_2O$	154-155* (3 mm)	1.4381	1.6252	86.09	11.30	42.48	42.88	75.5
 $\left[(C_6H_5)(C_2H_5)As\right]_2O$	191-192 (9 mm)	1.3564	1.6062	96.17	11.72	39.41	39.64	85.0
 $\left[(C_6H_5)(n\text{-}C_3H_7)As\right]_2O$	214-215 (10 mm)	1.2925	1.5900	106.02	12.03	36.58	36.89	90.0
 $\left[(C_6H_5)(n\text{-}C_4H_9)As\right]_2O$	231-232 (18 mm)	1.2460	1.5746	115.10	11.95	34.27	34.57	95.0

The reaction of methyl iodide with the n-propyl and n-butyl esters of phenylmethylarsenious acid, and also with some of the other phenylalkylarsenious acid esters, is more complex and proceeds with profound change as shown in the scheme:

TABLE 2

Formula of the ester	Boiling point	Pressure (in mm)	d_0^{20}	n_D^{20}	AR^{m}_{As}	Amount of As (in %)		Yield (in %)
						Found	Calculated	
$(C_6H_5)(CH_3)As-OCH_3$	95-96*	17	1.2975	1.5628	11.27	37.76	37.82	24.0
$(C_6H_5)(CH_3)As-OC_2H_5$	102-103	20	1.2473	1.5559	11.75	35.36	35.33	33.0
$(C_6H_5)(CH_3)As-OC_3H_7\text{-n}$	114-114.5	18	1.1987	1.5403	11.70	33.05	33.14	63.0
$(C_6H_5)(CH_3)As-OC_4H_9\text{-n}$	122-123	18	1.1675	1.5338	11.78	31.23	31.19	85.6
$(C_6H_5)(C_2H_5)As-OCH_3$	92-93	10	–	–	–	35.04	35.33	20.0
$(C_6H_5)(C_2H_5)As-OC_2H_5$	105-106	12	1.1980	1.5430	11.93	33.37	33.14	35.0
$(C_6H_5)(C_2H_5)As-OC_3H_7\text{-n}$	110-111	10	1.1692	1.5345	11.76	31.03	31.19	61.5
$(C_6H_5)(C_2H_5)As-OC_4H_9\text{-n}$	122-123	10	1.1448	1.5295	11.77	29.50	29.48	79.0
$(C_6H_5)(\text{n-}C_3H_7)As-OCH_3$	102-103	10	–	–	–	32.65	33.14	26.0
$(C_6H_5)(\text{n-}C_3H_7)As-OC_2H_5$	101-103	7	1.1700	1.5360	11.86	31.49	31.19	30.0
$(C_6H_5)(\text{n-}C_3H_7)As-OC_3H_7\text{-n}$	126.5-127	12.5	1.1397	1.5280	11.93	29.56	29.48	81.5
$(C_6H_5)(\text{n-}C_3H_7)As-OC_4H_9\text{-n}$	120-121	4	1.1253	1.5260	11.80	28.05	27.94	85.0
$(C_6H_5)(\text{n-}C_4H_9)As-OCH_3$	117-118	12	1.1747	1.5380	11.81	31.04	31.19	31.0
$(C_6H_5)(\text{n-}C_4H_9)As-OC_2H_5$	127-128	12	1.1454	1.5318	11.98	29.71	29.48	38.0
$(C_6H_5)(\text{n-}C_4H_9)As-OC_3H_7\text{-n}$	139-140	10	1.1158	1.5220	11.93	27.77	27.94	68.0
$(C_6H_5)(\text{n-}C_4H_9)As-OC_4H_9\text{-n}$	154-155	16.5	1.1038	1.5198	11.73	26.55	26.56	80.0



In addition to the addition products shown in Table 3, we isolated colorless crystalline substances from the reaction of ethyl iodide, n-propyl iodide or n-butyl iodide with the n-butyl esters of phenylmethyl-, phenyl-n-propyl- or phenyl-n-butylarsenious acid, which substances were not studied in more detail by us.

EXPERIMENTAL

The starting substance — phenyldichloroarsine — was prepared by the method of Sherlin and Bras [8]. Based on phenylhydrazine the product yield was 64%.

The bis(phenylalkylarsine) oxides needed for the synthesis of the phenylalkylarsenious acid esters were prepared by the method described earlier by one of us [7]; some of the data for these oxides are given in Table 1.

Preparation of Methyl Phenylmethylarsenite

In a flask with cap, filled with anhydrous copper sulfate, and reflux condenser was placed 33 g of bis(phenylmethylarsine) oxide and 18 ml of methyl alcohol. The flask contents were heated in a metal bath for 3 hours at 100-120°. After cooling the reaction mixture was transferred to an Arbuzov distillation flask.

Vacuum-distillation of the mixture gave two fractions: 1st with b. p. 91-103° (16 mm); 2nd with b. p. 154-156° (3 mm). Redistillation of the 1st fraction gave a substance with b. p. 95-96° at 17 mm.

Found %: As 37.76. $C_8H_{11}OAs$. Calculated %: As 37.82.

The isolated methyl ester of phenylmethylarsenious acid is a colorless liquid; the yield of pure ester was 24%.

$$d_4^{20}\ 1.2975,\ n_D^{20}\ 1.5628.$$

The fraction with b. p. 154-156° was unreacted bis(phenylmethylarsine) oxide.

Other esters of the phenylalkylarsenious acids were obtained by the described method, starting from the corresponding alcohols and bis(phenylalkylarsine) oxides.

The isolated esters are colorless liquids. They are readily soluble in acetone, ether, alcohol, dichloroethane and other organic solvents. Many of them have a sharp odor, irritating the mucous membrane of the nose and eyes. The obtained esters are characterized in Table 2.

Preparation of $C_6H_5(CH_3)As-OCH_3\cdot CuCl$. A mixture of 1.5 g of methyl phenylmethylarsenite with 0.8 g of cuprous chloride was prepared. The reaction proceeded with self-heating. The mixture crystallized on cooling. The crystals are soluble in hot benzene. After filtration the addition product was precipitated from benzene with ethyl ether. M. p. 70-72°.

Found %: Cl 11.45. $C_8H_{11}OAs\cdot CuCl$. Calculated %: Cl 11.93.

Preparation of $C_6H_5(C_4H_9)As-OCH_3\cdot CuCl$. A mixture of 1.5 g of the ester and 0.8 g of cuprous chloride was heated for 2 hours at 60°. The flask contents crystallized on cooling. After recrystallization from ethyl alcohol the substance melted at 40-41°. Greenish crystals, soluble in benzene, ether and alcohol.

Found %: Cl 10.09. $C_{11}H_{17}OAs.\cdot CuCl$. Calculated %: Cl 10.45.

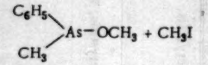
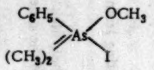
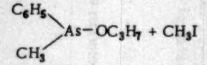
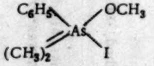
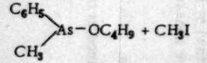
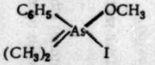
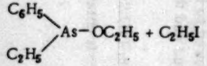
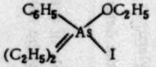
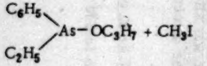
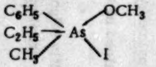
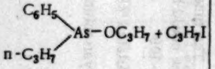
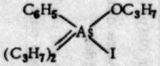
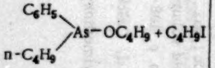
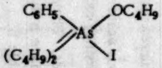
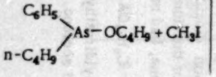
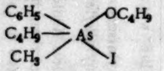
Addition of Methyl Iodide to Methyl Phenylmethylarsenite

A mixture of 7.5 g of methyl phenylmethylarsenite and 5.4 g of methyl iodide was sealed in a tube from which the air had been displaced by carbon dioxide (gas). The tube was allowed to stand at 19-20° for 60 hours. After several hours a slight contraction of the liquid volume could be detected and the appearance of crystals. The crystals, precipitated with ether from acetone, had m. p. 108-109°.

Found %: As 22.28; I 37.21. $C_9H_{14}OAsI$. Calculated %: As 22.08; I 37.29.

The addition product — phenyldimethylmethoxyarsonium iodide — is obtained as colorless crystals, soluble in water, alcohol, dichloroethane and acetone.

TABLE 3

Starting products	Reaction Temperature	Ratio of Reactants	Time) (in hrs)	Formula of obtained product	Melting point	% As		% I	
						Found	Calculated	Found	Calculated
 $(C_6H_5)(CH_3)As-OCH_3 + CH_3I$	19-20°	1:1	60		108-109°	22.28	22.08	37.21	37.29
 $(C_6H_5)(CH_3)As-OC_3H_7 + CH_3I$	20	1:1	120		109-110	22.42	22.08	37.32	37.29
 $(C_6H_5)(CH_3)As-OC_4H_9 + CH_3I$	40	1:1.8	10		109-110	22.37	22.08	37.39	37.29
 $(C_6H_5)(C_2H_5)As-OC_2H_5 + C_2H_5I$	100	1:1	8		111-113	19.72	19.61	33.21	33.17
 $(C_6H_5)(C_2H_5)As-OC_3H_7 + CH_3I$	20-30	1:2	120		112-114	21.12	21.15	35.63	35.81
 $(C_6H_5)(n\text{-}C_3H_7)As-OC_3H_7 + C_3H_7I$	140	1:1	5		162-163	17.45	17.66	30.27	29.91
 $(C_6H_5)(n\text{-}C_4H_9)As-OC_4H_9 + C_4H_9I$	130-150	1:1	16		135-136	16.13	16.07	27.63	27.20
 $(C_6H_5)(n\text{-}C_4H_9)As-OC_4H_9 + CH_3I$	20	1:1	5		139-141	17.97	17.66	30.40	29.91

Reaction of Methyl Iodide with n-Propyl Phenylmethylarsenite

A mixture of 8.1 g of n-propyl phenylmethylarsenite and 5 g of methyl iodide was sealed in a tube. The tube was allowed to stand at room temperature for 120 hours. The tube contents partially crystallized. The addition product was purified by its precipitation from acetone solution with anhydrous ether. M. p. 109-110°.

Found %: As 22.42; I 37.32. C_9H_{14} OAsI. Calculated %: As 22.08; I 37.29.

From the analysis data the obtained substance is phenyldimethylmethoxyarsonium iodide.

The reaction of other alkyl iodides with the esters of the phenylalkylarsenious acids was run in the same manner as described above. The data for the obtained substances are given in Table 3.

SUMMARY

1. It was shown that the reaction of alcohols with bis (phenylalkylarsine) oxides yields the corresponding phenylalkylarsenious acid esters in good yields. Sixteen new esters were synthesized by this method.

2. The reaction of cuprous chloride and of alkyl iodides with the esters of the phenylalkylarsenious acids was studied. The synthesis of 6 new arsonium salts is described.

3. It was established that the reaction of methyl iodide with the n-propyl and n-butyl esters of phenylmethylarsenious acid is quite complex and leads to the formation of phenyldimethylmethoxyarsonium iodide.

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* T. p. = C. B. Translation pagination.

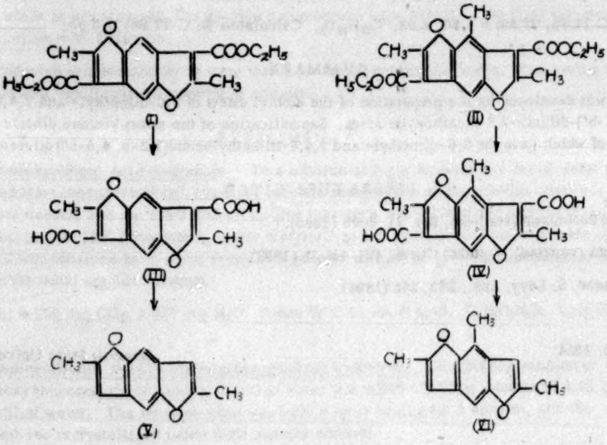
QUINONES

III. SYNTHESIS OF SUBSTITUTED BENZODIFURANS BY THE REACTION OF p-BENZOQUINONE AND TOLUQUINONE WITH ACETOACETIC ESTER

A. P. Terentyev, A. N. Grinev, and Pan Bon-Khvar

von Pechmann [1] was the first to establish that the reaction between p-benzoquinone and acetoacetic ester, in the presence of zinc chloride, leads to the formation of two crystalline compounds with m. p. 137 and 184°, corresponding to the empirical formulas $C_{12}H_{12}O_4$ and $C_{18}H_{18}O_6$. Later [2, 3] a scheme for this reaction was given, structural formulas for the substances obtained by von Pechmann were proposed, and the condensation of toluquinone with acetoacetic ester was also run. It was found that the yield of one of the substances obtained by von Pechmann, the benzofuran derivative, reaches 50% [2]. The yield of the other substance, the benzodifuran derivative, was not shown.

We selected such conditions for running the reaction as would predominantly give benzodifuran derivatives, and some of their transformations were realized. The condensation of p-benzoquinine and of toluquinone with acetoacetic ester gave the diethyl ester of 2,6-dimethylbenzo[1,2,-b, 4,5-b'] difuran-3,7-dicarboxylic acid (I) (yield 70%, based on the quinone) and the diethyl ester of 2,4,6-trimethylbenzo [1,2-b, 4,5-b'] difuran-3,7-dicarboxylic acid (II) (yield 60%), respectively. Saponification of the esters gave the earlier described [1,3] dibasic acids (III and IV), which under decarboxylation by heating with quinoline and copper oxide gave the previously unknown 2,6-dimethylbenzo[1,2-b, 4,5-b'] difuran (V) and 2,4,6-trimethylbenzo[1,2-b, 4,5-b'] difuran (VI) in good yields.



EXPERIMENTAL

Condensation of p-Benzoquinone with Acetoacetic Ester. To a solution of zinc chloride (28 g, 0.2 mole) in 28 g of anhydrous alcohol was added 39 g (0.3 mole) of the ester, and then with heating and stirring in 3-4 portions (over 5-10 minutes) was added 21 g (0.2 mole of p-benzoquinone. The flask contents were heated on the boiling water bath with constant stirring for 45 minutes, and then allowed to stand at room temperature for several hours. The obtained crystalline mass was separated and washed with a little ether. The crystalline benzodifuran derivative (I) had m. p. 184° (from a 1:1 mixture of dichloroethane and acetone). The yield of pure substance was 20.4 g (70%, based on p-benzoquinone). The mother liquor was diluted with water and allowed to stand for several hours. The water was decanted from the viscous semicrystalline precipitate and the precipitate was dissolved in ether. The ether extract was washed with water, then dried over calcium chloride, and evaporated. The obtained crystals were recrystallized from benzene. There was obtained 4.5 g of the benzofuran derivative with m. p. 137°, which melting point agrees with the literature [2]. The ester (I) was saponified with alcoholic caustic. The obtained sodium salt precipitate of the acid (III) was dissolved in water. Acidification with hydrochloric acid (to Congo) gave the acid (III).

Preparation of 2,6-Dimethylbenzo[1,2-b, 4,5-b'] difuran (V). A mixture of 2 g of the acid (III), 4.5 g of quinoline and 0.1 g of copper oxide was heated for 2 hours at 240-242° in a distillation flask. Then the temperature was raised and the flask contents were distilled. The distillate was acidified with dilute hydrochloric acid to acid reaction. The resulting crystals were filtered, and then purified by steam-distillation and one recrystallization from alcohol. The product (V) was obtained as white crystals with m. p. 113-114° and having a pleasant odor. The yield of the purified substance was 1.2 g.

Found %: C 77.22, 77.42; H 5.63, 5.65. $C_{12}H_{10}O_2$. Calculated %: C 77.40; H 5.41.

Condensation of Toluquinone with Acetoacetic Ester. The reaction was run the same as for p-benzoquinone. For reaction was taken 5 g (0.04 mole) of toluquinone, 6.5 g (0.05 mole) of acetoacetic ester, 5.5 g (0.04 mole) of zinc chloride and 5.5 g of anhydrous alcohol. The crystals obtained for the reaction were separated and recrystallized from a mixture of acetone and dichloroethane. The yield of purified benzodifuran derivative (II) was 3.2 g (60%, based on the quinone), m. p. 120-122°.

From the mother liquor was isolated 1 g of the benzofuran derivative with m. p. 173°, which melting point agrees with the literature [3]. Saponification of the ester (II) as before gave the acid (IV).

Preparation of 2,4,6-Trimethylbenzo[1,2-b, 4,5-b'] difuran (VI). For reaction was taken: acid (IV) 0.7 g, quinoline 2 g, copper oxide 0.1 g. The product (VI) was obtained as white crystals with m. p. 70-71.5° (from alcohol). Yield of purified substance 0.3 g.

Found %: C 77.83, 77.89; H 6.20, 6.03. $C_{13}H_{12}O_2$. Calculated %: C 77.98; H 6.05.

SUMMARY

A method was developed for the preparation of the diethyl esters of 2,6-dimethyl- and 2,4,6-trimethylbenzo[1,2-b, 4,5-b']-difuran-3,7-dicarboxylic acids. Saponification of the esters yielded dibasic acids, the decarboxylation of which gave the 2,6-dimethyl- and 2,4,6-trimethylbenzo[1,2-b, 4,5-b'] difurans.

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SYNTHESIS OF p-HYDROXYBENZENESULFONIC ACID DERIVATIVES

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The purpose of the present work was to synthesis the hydrazides of p-hydroxy- and p-ethoxybenzenesulfonic acids and a number of their derivatives, and also the derivatives of these acids with the complex-forming amines – ethylenediamine and phenylenediamine.

Usually the hydrazides of carboxylic acids are obtained by reacting either the esters or amides of the acids with hydrazine hydrate, but this method is not applicable to the preparation of the hydrazides of either p-hydroxy- or p-ethoxybenzenesulfonic acid. The esters of these acids are easily hydrolyzed in the presence of hydrazine hydrate and form hydrazine salts of the sulfonic acid. The amide group of sulfonic acids is not substituted by the hydrazide group even when heated in a sealed tube [1]; consequently, we obtained the hydrazides of p-hydroxy- and p-ethoxybenzenesulfonic acids by the reaction of the acid chlorides of these acids [2, 3] with hydrazine hydrate.

This reaction proceeds with good yield in aqueous medium; in nonaqueous solvents (alcohol, benzene, dioxane) the hydrazides are obtained in very low yields. The reaction of aqueous or alcoholic solutions of the hydrazides of p-hydroxy or p-ethaxybenzenesulfonic acid with aldehydes gave well-crystallized hydrazones.

The condensation of the acid chlorides of p-benzoyloxybenzenesulfonic acid or p-ethoxybenzenesulfonic acid with p-acetaminoaniline (4'-aminoacetanilide) in the presence of soda, followed by saponification of the reaction products with aqueous sodium hydroxide solution, gave p-hydroxy-p'-aminobenzenesulfonamilide and p-ethoxy-p'-aminobenzenesulfonanilide, respectively [4]. p-Bis(p-ethoxybenzenesulfonamido) benzene was obtained in the attempts made to condense p-ethoxybenzenesulfonyl chloride with p-phenylenediamine.

The condensation of p-benzoyloxybenzenesulfonyl chloride and p-ethoxybenzenesulfonyl chloride with aqueous solutions of N-acetylethylenediamine in the presence of soda [5] was used to prepare N-(β-aminoethyl)-p-hydroxy- and N-(β-aminoethyl)-p-ethoxybenzenesulfonamide, respectively.

As was revealed, the acid chlorides of these acids react very slowly with N-acetylethylenediamine in the absence of solvent, while in benzene solution the reaction proceeds quite rapidly. The final reaction products lend themselves to purification with difficulty.

All of the compounds synthesized by us were tested for their bactericidal action. The testing revealed that not one of them possessed significant antitubercular activity.

EXPERIMENTAL

p-Hydroxybenzenesulfonic Acid Hydrazide. To a solution of 5 g of hydrate in 5 ml of water was gradually added 10 g of p-benzoyloxybenzenesulfonyl chloride; here the temperature of the reaction mass was raised to 90°. Then the mixture was cooled, and the separated crystalline substance was filtered and recrystallized from water. Yield 4.5 g (71%); m. p. 160-165° (decompn.) After recrystallization from alcohol the hydrazide of p-hydroxybenzenesulfonic acid was obtained as a white crystalline powder with m. p. 165-166° (decompn.), readily soluble in acids, water, and the usual organic solvents.

3.735 mg sub.: 5.200 mg CO_2; 1.487 mg H_2O. Found %: C 37.99; H 4.45. $C_6H_8O_3N_2S$. Calculated %: C 38.29; H 4.28.

p-Hydroxybenzenesulfonic Acid (p-Hydroxybenzylidene) hydrazide. To a boiling solution of 1 g of the hydrazide of p-hydroxybenzenesulfonic acid in 20 ml of water was added a boiling solution of 0.65 g of p-hydroxybenzaldehyde in 5 ml of water. The reaction mass was cooled after boiling for 5 minutes, and the crystallized substance was filtered and recrystallized twice from aqueous alcohol.

The (p-hydroxybenzylidene)hydrazide of p-hydroxybenzene-sulfonic acid is a yellow crystalline powder with m. p. 148-149°, readily soluble in alcohol, acetone and ethyl acetate, and insoluble in benzene, ether and chloroform.

4.428 mg sub.: 8.100 mg CO_2; 1.750 mg H_2O. Found %: C 49.92; H 4.42. $C_{13}H_{12}O_4N_2S \cdot H_2O$. Calculated %: C 50.31; H 4.54. After drying over P_2O_5: 3.318 mg sub.: 6.432 mg CO_2; 1.178 mg H_2O. Found %: C 52.90; H 3.97; $C_{13}H_{12}O_4N_2S$. Calculated: C 53.44; H 4.13.

p-Hydroxybenzenesulfonic Acid (p-Acetaminobenzylidene)hydrazide. To a hot solution of 1 g of the hydrazide of p-hydroxybenzenesulfonic acid in 20 ml of water was added a solution of 0.9 g of p-acetaminobenzaldehyde in 15 ml of water. The mixture was heated at the boil for 5 minutes, and the substance crystallized on cooling. After two recrystallizations from aqueous alcohol the (p-acetaminobenzylidene)hydrazide of p-hydroxybenzenesulfonic acid was obtained as an orange crystalline powder with m. p. 184-185° (decompn.), readily soluble in alcohol, acetone and ethyl acetate, and poorly soluble in benzene and ether.

4.409 mg sub.: 8.711 mg CO_2; 1.960 mg H_2O. Found %: C 53.91; H 4.97. $C_{15}H_{15}O_4N_3S$. Calculated %: C 54.04; H 4.53.

P-Hydroxybenzenesulfonic Acid (p-Dimethylaminobenzylidene)hydrazide. To a hot solution of 1 g of the hydrazide of p-hydroxybenzenesulfonic acid in 30 ml of anhydrous alcohol was added 0.8 g of p-dimethylaminobenzaldehyde and the mixture was boiled for 5 minutes. After long cooling a grayish-green substance crystallized. After two recrystallizations from 25% acetic acid the (p-dimethylaminobenzylidene)hydrazide of p-hydroxybenzenesulfonic acid was obtained as a pinkish crystalline substance with m. p. 157-158° (decompn.), readily soluble in alcohol, acetone and chloroform.

3.431 mg sub.: 7.101 mg CO_2; 1.660 mg H_2O. Found %: C 56.48; H 5.41. $C_{15}H_{17}O_3N_3S$. Calculated %: C 56.42; H 5.36.

p-Ethoxybenzenesulfonic acid Hydrazide. To a solution of 10 g of hydrazine hydrate in 10 ml of water was gradually added 20 g of p-ethoxybenzenesulfonyl chloride. On conclusion of addition the hot reaction mass was cooled, the crystallized substance filtered, washed with ice water, and recrystallized from water. There was obtained 15 g (76%) of the hydrazide of p-ethoxysulfonic acid with m. p. 109-111° (decompn). Recrystallization from anhydrous alcohol gave white lustrous needles with m. p. 111° (decompn.), readily soluble in the ordinary organic solvents.

8.800 mg sub.: 1.025 ml N_2 (25°, 731 mm). Found %: N 12.83. $C_8H_{12}O_3N_2S$. Calculated %: N 12.95.

p-Ethoxybenzenesulfonic Acid (p-Acetaminobenzylidene)hydrazide. To a hot solution of 2 g of the hydrazide of p-ethoxybenzenesulfonic acid in 40 ml of water was added a solution of 1.35 g of p-acetaminobenzaldehyde in 25 ml of water, and the mixture was boiled for 5 minutes. Then the solution was cooled; the separated crystalline substance was filtered and then recrystallized twice from alcohol. The (p-acetaminobenzylidene)hydrazide of p-ethoxybenzenesulfonic acid was obtained as a white crystalline powder with m. p. 186-186.5° (decompn.), readily soluble in acetone and acetic acid, and insoluble in dichloroethane and chloroform.

3.673 mg sub.: 7.642 mg CO_2; 1.750 mg H_2O. Found %: C 56.78; H 5.33. $C_{17}H_{19}O_4N_3S$. Calculated %: C 56.49; H 5.29.

p-Ethoxybenzenesulfonic Acid (p-Dimethylaminobenzylidene)-hydrazide. To a hot solution of 2 g of the hydrazide of p-ethoxybenzenesulfonic acid in 10 ml of anhydrous alcohol was added 1.6 g of p-dimethylaminobenzeldehyde. The (p-dimethylaminobenzylidene)hydrazide of p-ethoxybenzenesulfonic acid that separated on standing was recrystallized from alcohol to give a white crystalline powder with 170-171° (decompn.), soluble in acetone, alcohol, acetic acid, chloroform and dichloroethane.

3.590 mg sub.: 7.738 mg CO_2; 1.969 mg H_2O. Found %: C 58.82; H 6.13. $C_{17}H_{21}O_3N_3S$. Calculated %: C 58.76; H 6.09.

p-Ethoxybenzenesulfonic Acid (4-Hydroxy-3-methoxybenzylidene)hydrazide. To a hot solution of 2 g of the hydrazide of p-ethoxybenzenesulfonic acid in 40 ml of water was added a solution of 1.7 g of vanillin in 35 ml of water, and the mixture was boiled for 5 minutes. The separated oily substance solidified on standing.

The (4-hydroxy-3-methoxybenzylidene)hydrazide of p-ethoxybenzenesulfonic acid was recrystallized twice from dilute acetic acid to give a white crystalline powder with m. p. 128-130° (decompn.), readily soluble in alcohol, acetone and chloroform.

3.524 mg sub.: 7.124 mg CO_2; 1.572 mg H_2O. Found %: C 55.17; H 4.99. $C_{16}H_{18}O_5N_2S$. Calculated %: C 54.84; H 5.17.

p-Ethoxy-p'-aminobenzenesulfonanilide. A mixture of 16 g of p-acetaminoaniline, 24 g of p-ethoxybenzenesulfonyl chloride, 17 g of soda and 80 ml of water was stirred at room temperature for 6 hours, after which it was heated at 40° for 1 hour. The resulting p-ethoxy-p'-acetaminobenzenesulfonanilide was filtered, washed with water, and saponified by boiling with 100 ml of 20% aqueous sodium hydroxide solution for 2 hours. Then the solution was diluted with an equal volume of water and acidified with acetic acid. The separated p-ethoxy-p'-aminobenzenesulfonanilide was dissolved with heating in 250 ml of water made acid with hydrochloric acid, decolorized, and made alkaline with saturated sodium bicarbonate solution. The p-ethoxy-p'-aminobenzenesulfonanilide was obtained as a whitish crystalline powder with m. p. 155-156°, soluble in alcohol, chloroform and acetone.

3.280 mg sub.: 6.941 mg CO_2; 1.587 mg H_2O. Found %: C 57.75; H 5.41. $C_{14}H_{16}O_3N_2S$. Calculated %: C 57.52; H 5.51.

p-Hydroxy-p'-aminobenzenesulfonanilide. A mixture of 10 g of p-acetaminoaniline, 19.4 g of p-benzoyloxybenzenesulfonyl chloride, 10 g of soda and 50 ml of water was stirred at room temperature for 5 hours. On conclusion of reaction the precipitate was filtered, washed with water, and saponified by boiling with 150 ml of 20% aqueous sodium hydroxide solution for 2 hours. Then the solution was acidified with acetic acid. The separated p-hydroxy-p'-aminobenzenesulfonanilide was dissolved with heating in 100 ml of water made acid with hydrochloric acid, decolorized, and then made alkaline with saturated sodium bicarbonate solution. After two recrystallizations from water the p-hydroxy-p'-aminobenzenesulfonanilide was obtained as a whitish crystalline powder with m. p. 200-201°, soluble in alcohol and acetone, and insoluble in ether and chloroform.

3.959 mg sub.: 7.945 mg CO_2; 1.662 mg H_2O. Found %: C 54.77; H 4.69. $C_{12}H_{12}O_3N_2S$. Calculated %: C 54.53; H 4.58.

p-Bis(p-ethoxybenzenesulfonamido)benzene. To a solution of 15 g of phenylenediamine in 50 ml of water was added 9 g of p-ethoxybenzenesulfonyl chloride, and the mixture was stirred for 2.5 hours at 45°. Then the reaction mass was made alkaline, the separated phenylenediamine removed, and from the alkaline solution after acidification a substance, difficultly soluble in the ordinary organic solvents, was isolated. After recrystallization from glacial acetic acid and then from nitrobenzene the substance was obtained as a fine crystalline violet powder with m. p. 246° (decompn).

3.701 mg sub.: 7.519 mg CO_2; 1.721 mg H_2O. Found %: C 55.44; H 5.20 $C_{22}H_{24}O_6N_2S_2$. Calculated %: C 55.44; H 5.10.

N-(β-Aminoethyl)-p-hydroxybenzenesulfonamide. To a solution of 3.75 g of N-acetylethylenediamine and 4.5 g of soda in 50 ml of water was added a solution of 12 g of p-benzoyloxybenzenesulfonyl chloride in 50 ml of benzene, and the mixture was stirred at 50° for 3 hours. Then the benzene and part of the water was distilled off, and the obtained precipitate filtered and washed with water. The substance was saponified by boiling with 60 ml of 20% aqueous hydrochloric acid solution for 26 hours. On conclusion of reaction the benzoic acid was removed, the filtrate evaporated *in vacuo*, and the residue recrystallized thrice from concentrated hydrochloric acid. A white crystalline powder with m. p. 240-243° (decompn.) was obtained, readily soluble in water, and poorly soluble in alcohol.

15.565 mg sub.: 1.5 ml N_2 (25°, 757 mm). 9.120 mg sub.: 1.82 ml 0.02 N $AgNO_3$. Found %: N 10.98; Cl 14.15. $C_8H_{12}O_3N_2S \cdot HCl$. Calculated %: N 11.08; Cl 14.02.

N-(β-Aminoethyl)-p-ethoxybenzenesulfonamide. To a solution of 3.75 g of N-acetylethylenediamine and 4.5 g of soda in 50 ml of water was added a solution of 9 g of p-ethoxybenzenesulfonyl chloride in 50 ml of benzene. The mixture was heated at 50° for 3.5 hours. The substance obtained after distilling off the benzene was separated, washed with water, and saponified by boiling with 45 ml of 20% aqueous hydrochloric acid solution for 26 hours. On conclusion of reaction the solution was evaporated, and the residue was recrystallized twice from anhydrous alcohol and then from concentrated hydrochloric acid. White crystalline powder with m. p. 236° (decompn.), readily soluble in water, and moderately soluble in alcohol.

33.733 mg sub.: 6.16 ml 0.02 N $AgNO_3$. 4.506 mg sub.: 0.400 ml N_2 (19°, 734 mm). Found %: Cl 12.95; N 10.02. $C_{10}H_{16}O_3N_2S \cdot HCl$. Calculated %: Cl 12.63; N 9.97.

SUMMARY

The following were synthesized: 1) the hydrazide of p-hydroxybenzenesulfonic acid and from it the corresponding hydrazones with p-hydroxybenzaldehyde, p-acetaminobenzaldehyde, and p-dimethylaminobenzaldehyde; 2) the hydrazide of p-ethoxybenzenesulfonic acid and from it the corresponding hydrazones with p-acetaminobenzaldehyde, p-dimethylaminobenzaldehyde and vanillin; 3) the p-aminoanilides of p-ethoxy- or p-hydroxybenzenesulfonic acid and p-bis(p-ethoxybenzenesulfonamido)benzene; 4) N-(β-aminoethyl)-p-hydroxybenzenesulfonamide and N-(β-aminoethyl)-p-ethoxybenzenesulfonamide.

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PREPARATION OF TRIMETHYLFURFURYLAMMONIUM SALTS

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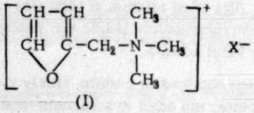
Some of the salts of quaternary ammonium bases, containing the furan or tetrahydrofuran ring, are used as medicinals [1]. At the present time the trimethylfurfuryl ammonium salts (I) find use in medicine as substitutes for pilocarpine.



(I)

Trimethylfurfurylammonium Iodide (I, X = I) is sold under the name of "furamon" in the Soviet Union and is used for the treatment of glaucoma (instead of the imported pilocarpine) [2], and also in veterinary practice [3]. Two methods for its preparation are described in the literature: directly from furfurylamine [4] or through dimethylfurfurylamine [1, 5].

We developed a method for the preparation of trimethylfurfurylammonium iodide in 60% yield, while according to the literature this product is obtained in a yield of only 25%. This method served as the basis for the production of "furamon" [6].

The starting material is furfural (2-furaldehyde), which by the method of reductive amination is converted into furfurylamine [7]. The furfurylamine was exhaustively methylated with methyl iodide in the presence of potassium carbonate. The purification, and also the properties of the trimethylfurfurylammonium iodide obtained here, are given in the experimental part.

Instead of methyl iodide we also used other, less expensive, methylating agents and synthesized the trimethylfurfurylammonium methyl sulfate and benzenesulfonate.

Trimethylfurfurylammonium Methyl Sulfate (I, X = SO_4CH_3) is formed when furfurylamine is reacted with dimethylsulfate in the presence of potassium carbonate. The reaction product is a nearly colorless crystalline substance, very hydroscopic, easily soluble in water and alcohol, and insoluble in diethyl ether and the esters. Its aqueous solutions show neutral, decolorized bromine water, and form a precipitate with barium chloride solution only after boiling with alkali. The elementary analysis data for sulfur and nitrogen support the empirical formula $C_9H_{17}O_5NS$. We were unable to determine the amount of carbon and hydrogen due to the extreme hygroscopicity of the salt. For the same reason the melting point determinations gave very ill-defined results (66-71°).

We also prepared trimethylfurfurylammonium methyl sulfate from trimethylfurfurylammonium iodide and dimethyl sulfate [8]. The salt obtained here was identical in all of its properties with the above-described salt. Due to its unusually great hygroscopicity this salt could not find use in medical practice.

Trimethylfurfurylammonium Benzenesulfonate (I, X = $SO_3C_6H_5$) is not described in the literature. We prepared it from furfurylamine and methyl benzenesulfonate. It is interesting to mention that irrespective of the molar ratios of reactants used, only the salt of the quaternary ammonium base, in greater or less yield, is always formed. This is observed irrespective of whether an alkaline, acid or neutral medium is used; neither the secondary nor the tertiary amine could be obtained by this method.

Trimethylfurfurylammonium benzenesulfonate is a colorless crystalline substance, easily soluble in water and alcohol, and insoluble in diethyl ether, benzene and the esters. Its aqueous solution reacts neutral and decolorizes bromine water. M. p. 134-135°. The elementary analysis data support the decomposition $C_{11}H_{19}O_4NS$. The salt, in contrast to the methyl sulfate, is not hygroscopic, and consequently it can find use in medical practice as a substitute for the more expensive quaternary iodide [9].

All three trimethylfurfurylammonium salts described here are close to each other in their curative action and toxicity.

EXPERIMENTAL

1. Synthesis of Trimethylfurfurylammonium Iodide. In a round-bottomed flask, fitted with dropping funnel, thermometer, reflux condenser and stirrer, was placed 9.7 g (0.1 mole) of furfurylamine, 100 ml of water and 15 g of chemically pure, finely pulverized potassium carbonate. With cooling in a water bath and mechanical stirring to the solution was added dropwise 50 g (0.35 mole) of methyl iodide, with maintenance of the temperature inside the mass at 15-20°; the reaction mass was carefully heated to 40-45° and maintained at this temperature for 3 hours, after which the excess methyl iodide was distilled off.

The reaction mass was steam-distilled until the escaping condensate showed neutral, decolorized with charcoal, evaporated to dryness, and dried to complete moisture removal in a vacuum-oven at 80° or in a vacuum-desiccator over calcium chloride or silica gel. The dried mixture of salts was extracted with 25-30 ml of anhydrous alcohol, and from the solution the trimethylfurfurylammonium iodide was precipitated with either 200 ml of anhydrous ethyl acetate or 150 ml of anhydrous butyl acetate.

The trimethylfurfurylammonium iodide was obtained as a white, finely crystalline, lustrous precipitate; it was separated, washed with anhydrous ethyl acetate, and dried in a vacuum-desiccator to constant weight. The yield was 16 g (60%), based on furfurylamine. M. p. 118-120°; from its iodine content, determined argentometrically, the substance calculated as 99.8% trimethylfurfurylammonium iodide.

2. Synthesis of Trimethylfurfurylammonium Methyl Sulfate. To a solution of furfurylamine (9.7 g, 0.1 mole) in 150 g of an aqueous 10% potassium carbonate solution at 15-20° was added in drops and with stirring 41 g (0.32 mole) of dimethyl sulfate. Then the liquid was heated to 40-45° and stirred at this temperature for 1 hour. The reaction mass was steam-distilled until the condensate showed neutral; the residue was decolorized with charcoal, evaporated, and dried to constant weight in a vacuum-desiccator over either silica gel or sulfuric acid. The dry residue was extracted with 55 ml of anhydrous alcohol, the alcohol vacuum-distilled, and the residue dried to constant weight in a vacuum-desiccator. The substance slowly solidified during the drying process, forming coarse, transparent, colorless or slightly yellowish crystals. Yield 17-17.5 g (68-70%). M. p. 66-71° (the substance was heated in a test tube, with the thermometer inside the mass). When heated over a free flame the substance darkens and decomposes with the evolution of trimethylamine.

0.3316 g sub.: 0.3064 g $BaSO_4$ [10]. 0.2413 g sub.: 0.2256 g $BaSO_4$. 0.4710 g sub.: 18.27 ml 0.1 N H_2SO_4. 0.5931 g sub.: 24.26 ml 0.1 N H_2SO_4. Found %: S 12.70, 12.84; N 5.43, 5.72. $C_9H_{17}O_5NS$. Calculated %: S 12.74; N 5.58.

We also synthesized the trimethylfurfurylammonium methyl sulfate from trimethylfurfurylammonium iodide and dimethyl sulfate by the method of gradually adding dimethyl sulfate (10 g) to trimethylfurfurylammonium iodide (20 g), with heating on the water bath. The substance obtained here was identical with the substance described above.

3. Synthesis of Trimethylfurfurylammonium Benzenesulfonate [6]. To a 10% aqueous solution of potassium carbonate (15 g) was added 11.7 g of furfurylamine, and with stirring and cooling (15-20°) was added in drops 62.5 g (3 mol. equivs.) of methyl benzenesulfonate. The liquid was stirred for 1 hour at 20° and then for another hour at 45°. The rest of the procedure was the same as described above for the preparation of the quaternary methyl sulfate. The dried mixture of salts was recrystallized from 120 ml of an alcohol-butyl acetate (1:4) mixture. Yield 18 g (50%). M. p. 134-135°.

0.1186 g sub.: 0.2437 g CO_2; 0.0706 g H_2O. 0.1154 g sub.: 0.2368 g CO_2; 0.0683 g H_2O. 0.1070 g sub.: 4.7 ml N_2 (26°, 738 mm). 0.1233 g sub.: 5.2 ml N_2 (23°, 742 mm). Found %: C 56.07, 56.00; H 6.66, 6.62; N 4.87, 4.7 4.74. $C_4H_{19}O_4NS$. Calculated %: C 56.56; H 6.40; N 4.71.

SUMMARY

1. It was shown that the reaction of furfurylamine with methyl iodide in aqueous potassium carbonate solution gives trimethylfurfurylammonium iodide in 60% yield.

2. The reaction product from furfurylamine and dimethyl sulfate, identified as trimethylfurfurylammonium methyl sulfate, was isolated and characterized.

3. The reaction product from furfurylamine and methyl benzenesulfonate, identified as trimethylfurfurylammonium benzenesulfonate, was isolated and characterized.

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SYNTHESIS OF DIASTEREOISOMERIC α-PHENYL-β-(4-PIPERIDYL)-GLUTARIC ACIDS

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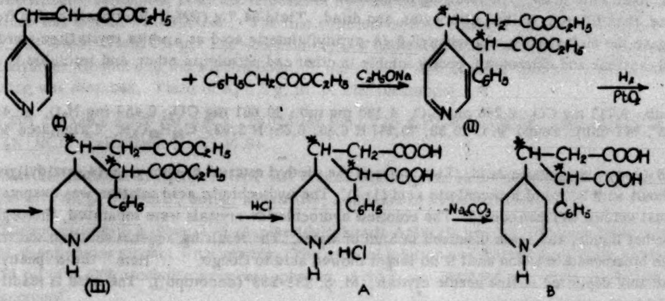
The present work was devoted to the synthesis and study of the properties of the diastereoisomeric α-phenyl-β-(4-piperidyl)-glutaric acids. Similar compounds are of interest as starting substances for the synthesis of 2,3-disubstituted quinuclidine derivatives by our earlier described method [1]. The diastereoisomeric α-phenyl-β-(4-piperidyl)-glutaric acids were obtained by the following scheme:



The ethyl ester of β-(4-pyridyl)acrylic acid (I) was condensed at 60° with the ethyl ester of phenylacetic acid in the presence of an equivalent amount of sodium ethylate; here the diethyl ester (II) of α-phenyl-β-(4-pyridyl)-glutaric acid was obtained in 90% yield. Compound (II) and all of the substances obtained from it, presented in the scheme, contain two asymmetric carbon atoms, which indicates the existence of two diastereoisomeric forms for these compounds.

The reduction of the hydrochloride of the diester (II) in alcoholic solution at room temperature in the presence of platinum catalyst (according to Adams) leads to the formation of the hydrochloride of the diethyl ester of α-phenyl-β-(4-piperidyl)-glutaric acid. Treatment of an aqueous solution of the obtained hydrochloride with 10% sodium carbonate solution gave colorless crystals, being the crystallohydrate of the diester (III). The latter when vacuum-distilled loses a mole of water, being converted into a colorless viscous liquid, which readily adds a mole of water in the air, again forming the crystallohydrate. The hydrochlorides of α-phenyl-β-(4-piperidyl)-glutaric acid (A) were obtained when the diethyl ester (III) of α-phenyl-β-(4-piperidyl)-glutaric acid was heated with concentrated hydrochloric acid. Two diastereoisomeric forms of the hydrochloride were isolated: 1) hydrochloride A_1: m. p. 230-231° (decompn.), and 2) hydrochloride A_2: m. p. 178°, differing, in addition to the melting point, also in its solubility in water. Hydrochloride A_2 is considerably more soluble in water than in hydrochloride A_1, and consequently it can be isolated only after the water from the removal of hydrochloride A_1 is completely evaporated.

The free diastereoisomeric acids (B) were obtained by treating the hydrochloride solutions of the corresponding acids in anhydrous alcohol with the calculated amount of alcoholic ammonia solution. From hydrochloride A_1 was isolated the free acid B_1 with m. p. 210-212°, and from hydrochloride A_2 the free acid B_2 with m. p. 272°. Acid B_1 is converted into the diastereoisomeric acid B_2 when heated in vacuo at 230-240°.

The reaction of bromine with the diethyl ester of α-phenyl-β-(4-piperidyl)-glutaric acid (III) was studied for the purpose of obtaining the diethyl ester of α-phenyl-α-bromo-β-(4-piperidyl)-glutaric acid. Compound (III) was treated with bromine at room temperature in chloroform solution. Instead of the expected bromo derivative the hydrobromide of the perbromide of the diethyl ester of α-phenyl-β-(4-piperidyl)-glutaric acid was obtained as bright yellow crystals. The hydrobromide of the perbromide failed to decompose when boiled in chloroform solution for 5 hours, and also when heated without solvent to 145°. Treatment of the hydrobromide of the perbromide with 50% potash solution in the cold gave the free perbromide as a colorless oil with a strong halogen odor. The perbromide is easily converted into the original substance (III) when shaken with acetone or when heated with 50% potash solution.

We were also unable to obtain the diethyl ester of α-phenyl-α-bromo-β-(4-piperidyl)glutaric acid in the bromination of compound (III) with bromine in boiling acetic acid, or with dibromodioxane in chloroform or acetic acid solution at the boil. In these experiments the diester (III) remained unchanged.

EXPERIMENTAL

Diethyl α-Phenyl-β-(4-pyridyl)glutarate (II). To the sodium ethylate obtained from 2.6 g of metallic sodium and 40 ml of anhydrous alcohol was added 18.56 g of ethyl phenylacetate and 20 g of ethyl β-(4-pyridyl)-acrylate. The reaction mass was heated for 2 hours at 60°. Here the yellow homogeneous solution was converted into a dense, brown-colored solid mass. The resulting precipitate was treated with 300 ml of water containing 8 ml of glacial acetic acid, then filtered, washed with water, and dried. Yield 34.7 g (90%). Recrystallization from petroleum ether gave the diethyl ester of α-phenyl-β-(4-pyridyl)glutaric acid as a white crystalline powder, readily soluble in alcohol, acetone and chloroform, poorly soluble in ether and petroleum ether, and insoluble in water. M. p. 100°.

3.768 mg sub.: 9.711 mg CO_2; 2.290 mg H_2O. 4.130 mg sub.: 10.661 mg CO_2; 2.459 mg H_2O. 12.465 mg sub.: 0.431 ml N_2 (20.5°, 741 mm). Found %: C 70.33, 70.44; H 6.80, 6.65; N 3.92. $C_{20}H_{23}O_4N$. Calculated %: C 70.38; H 6.74; N 4.11.

α-Phenyl-β-(4-pyridyl)glutaric Acid. Two grams of the diethyl ester of α-phenyl-β-(4-pyridyl)glutaric acid was boiled for 4 hours with 20 ml of hydrochloric acid (1:1). The hydrochloric acid solution was evaporated to a fourth of its original volume and then cooled. The colorless hydrochloride crystals were separated, thoroughly pressed free of mother liquor, and again dissolved in 5 ml of water. The resulting aqueous solution was treated with a saturated sodium bicarbonate solution until it no longer showed acid to Congo. Here the α-phenyl-β-(4-pyridyl)glutaric acid deposited as fine needle crystals. M. p. 231-233° (decompn.). The acid is readily soluble in water and insoluble in organic solvents.

3.746 mg sub.: 9.223 mg CO_2; 1.819 mg H_2O. Found %: C 67.19; H 5.43. $C_{16}H_{15}O_4N$. Calculated %: C 67.37; H 5.26.

Diethyl α-Phenyl-β-(4-piperidyl)glutarate (III). To a solution of 28.3 g of diethyl α-phenyl-β-(4-pyridyl) glutarate in 235 ml of anhydrous alcohol was added 13.8 ml of a 22% alcoholic hydrogen chloride solution. The resulting alcohol solution of the hydrochloride of diethyl %-phenyl-β-(4-pyridyl)glutarate was hydrogenated at room temperature in the presence of 0.8 g of platinum oxide. The necessary amount of hydrogen was absorbed in 140 hours. Then the alcohol solution was filtered from the platinum black and evaporated in vacuo to dryness. The hydrochloride (III) was obtained in quantitative yield.

To obtain the free base the aqueous hydrochloride solution was treated with 10% soda solution until it showed alkaline to phenolphthalein. The resulting precipitate was filtered, washed with water, and dried. The crystallohydrate (III) was obtained as thin colorless needles (from acetone), readily soluble in alcohol and chloroform, and poorly soluble in ether, acetone and water. M. p. 79-80°.

2.875 mg sub.: 6.890 mg CO_2; 2.109 mg H_2O. 5.296 mg sub.: 1.53 ml 0.01 N H_2SO_4. Found %: C 65.40; H 8.20; N 4.04. $C_{20}H_{29}O_4N \cdot H_2O$. Calculated %: C 65.72; H 8.50; N 3.98.

The obtained crystallohydrate (III) was vacuum-distilled without decomposition, losing here a mole of water of crystallization. B. p. 172° at 0.1 mm. Colorless, exceedingly viscous liquid, which slowly crystallized in the air, reverting back to the above described crystallohydrate with m. p. 80°.

3.740 mg sub.: 9.448 mg CO_2; 2.849 mg H_2O. Found %: C 68.94; H 8.52. $C_{20}H_{29}O_4N$. Calculated %: C 69.14; H 8.36.

Diethyl α-Phenyl-β-(4-N-acetylpiperidyl)glutarate. The hydrochloride (III) (2.1 g) was treated with 10 ml of 50% aqueous potash solution and then extracted with chloroform. The chloroform solution was dried over potash, the chloroform distilled in vacuo, and the residue heated with 20 ml of acetic anhydride for 1 hour. The acetic anhydride was vacuum-distilled, the residue dissolved in ether, the ether solution washed with water, then with 10%

soda solution, and dried over potash. After removing the ether the substance was vacuum-distilled. B. p. 215-218° (0.3 mm). Exceedingly viscous colorless liquid that crystallized on standing. Yield 1.5 g (70.4%). M. p. 85°. The substance is readily soluble in ether, chloroform and alcohol, and difficultly soluble in water.

3.659 mg sub.: 9.150 mg CO_2; 2.619 mg H_2O. 3.311 mg sub.: 8.331 mg CO_2; 2.456 mg H_2O. Found %: C 68.24, 68.25; H 8.00, 8.25. $C_{22}H_{31}O_5N$. Calculated %: C 67.86; H 8.17.

α-Phenyl-β-(4-piperidyl)glutaric Acid Hydrochlorides (A_1 and A_2). A mixture of 0.9 g of diethyl α-phenyl-β-(4-piperidyl)glutarate and 9 ml of concentrated hydrochloric acid was boiled for 15 hours. The hydrochloric acid solution was decolorized with charcoal and evaporated on the water bath to incipient crystallization. The colorless crystals obtained on cooling were separated and washed with acetone. Yield of A_1 0.3 g; m. p. 230-231° (decompn).

3.835 mg sub.: 8.243 mg CO_2; 2.453 mg H_2O. 9.860 mg sub.: 0.385 ml N_2 (20°, 727 mm); 5.497 mg sub.: 0.85 ml 0.01 N $AgNO_3$. Found %: C 58.74; H 7.16; N 4.35; Cl 10.97. $C_{16}H_{21}O_4N \cdot HCl$. Calculated %: C 58.98; H 6.74; N 4.28; Cl 10.84.

The filtrate, remaining after the removal of hydrochloride A_1, was evaporated in vacuo to dryness, and the oily residue was rubbed with acetone. The fine colorless crystals obtained here were separated, washed with acetone, and dried. Yield 0.4 g. The obtained crystals melted in the range 170-212°. They were dissolved in 7 ml of anhydrous alcohol and the alcohol solution was diluted with 16 ml of anhydrous ether. An oil that crystallized on standing was obtained. Yield of A_2 0.2 g, m. p. 178° (decompn).

3.991 mg sub.: 1.735 mg AgCl. 17.014 mg sub.: 2.55 ml 0.02 N $AgNO_3$. Found %: Cl 10.75, 10.63. $C_{16}H_{21}O_4N \cdot HCl$. Calculated %: Cl 10.84.

After the removal of A_2 the filtrate was diluted with another 40 ml of anhydrous ether to give 0.17 g of substance with m. p. 208-212°, being, apparently, a mixture of hydrochlorides A_1 and A_2.

Diastereoisomeric α-Phenyl-β-(4-piperidyl)glutaric Acids (B_1 and B_2). Hydrochloride A_1 (0.2 g) was dissolved in 12 ml of anhydrous alcohol with heating. The alcohol solution was filtered from some turbidity and then treated with 0.23 ml of 4.48% alcoholic ammonia solution. Acid B_1 was obtained as a white crystalline powder. M. p. 210-212° (decompn).

A_2 (0.2 g) was treated with the same manner. Acid B_2 was obtained. M. p. 272° (decompn).

4.116 mg sub.: 9.954 mg CO_2; 2.671 mg H_2O. 8.560 mg sub. 0.374 ml N_2 (23°, 736 mm). Found %: C 66.00; H 7.26; N 4.88. $C_{16}H_{21}O_4N$. Calculated %: C 65.98; H 7.22; N 4.82.

Conversion of Acid B_1 Into Acid B_2. Hydrochloride A_1 (m. p. 230-231°) (0.2 g) was heated in vacuo (20 mm) at 230-235° for 15 minutes. The glassy mass obtained here was dissolved in 2 ml of anhydrous alcohol, the alcohol solution decolorized with charcoal, and then diluted with 10 ml of anhydrous ether. The resulting precipitate was separated, dissolved in 0.8 ml of saturated bicarbonate solution, and the thus obtained solution treated with acetic acid. There was obtained 0.07 g of acid B_2 as fine colorless crystals, readily soluble in water. M. p. 272° (decompn.).

Diethyl α-Phenyl-β-(4-piperidyl)glutarate Perbromide Hydrobromide. To a solution of 17.5 g of the hydrochloride of the diethyl ester of α-phenyl-β-(4-piperidyl)glutaric acid in 54 ml of dry chloroform was added at 20° with stirring over 8 hours a solution of 7.32 g of bromine in 55 ml of chloroform. Toward the end of bromine addition the solution became dark red in color, which color failed to vanish in the next 16 hours. The reaction mass was evaporated to a volume of 40 ml and then diluted with 100 ml of dry ether. The hydrobromide of the perbromide of (III) precipitated as bright yellow crystals, m. p. 145-147° (decompn). The hydrobromide of the perbromide of (III) is readily soluble in chloroform, alcohol and acetone, and insoluble in ether and water.

3.130 mg sub.: 4.698 mg CO_2; 1.370 mg H_2O. 3.317 mg sub.: 4.964 mg CO_2; 1.550 mg H_2O. 9.690 mg sub.: 0.206 ml N_2 (27°, 729 mm). 3.274 mg sub.: 3.141 mg AgBr. Found %: C 40.96; 40.84; H 4.90, 5.23; N 2.32; Br 40.83. $C_{20}H_{30}O_4NBr_3$. Calculated %: C 40.82; H 5.1; N 2.38; Br 40.82.

SUMMARY

The synthesis of the diastereoisomeric α-phenyl-β-(4-piperidyl)glutaric acids was realized, and also their mutual interconversion.

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* T. p. = C. B. Translation pagination.

THE SYNTHESIS OF SOME 4-BIPHENYLAMINE DERIVATIVES

S. Sh. Rozina and R. P. Lastovsky

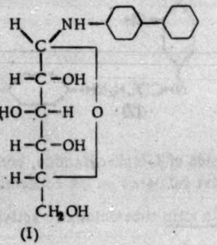
Quite a few papers have been published in recent years on the synthesis of organic compounds possessing activity against tubercle bacilli. As is known, some of the substances proved to be extremely effective and found use in the chemotherapy of tuberculosis, in which number 4-aminosalicyclic acid is included [1]. Also, many derivatives of 4-aminosalicylic acid were prepared and tested [2-4].

There is an indication that the activity of 4-biphenylamine is nearly 20 times greater than that of 4-aminosalicylic acid [2]. However, 4-biphenoylamine is hardly suitable for use in view of its toxicity and ease of oxidation.

It was of interest to protect the amino group of 4-biphenylamine for the purpose of obtaining a more stable and less toxic compound, and also to realize the synthesis of 4-biphenylamine derivatives by its condensation with 4-aminosalicylic acid. Glucose was selected to protect the amino group in 4-biphenylmine.

Depending on the synthesis conditions, the condensation of aromatic amines with glucose proceeds either between the amino group and the hydroxyl at the glucosidic carbon with the formation of glucosylarylamines, or in the case of using more drastic synthesis conditions between the amino group and the oxygen of the aldehyde group with the formation of azomethines. The latter are readily decomposed by alkalies, while the glucosylarylamines are unstable toward acids [5, 6].

The glucoside (I) of 4-biphenylamine is not reported in the literature. It was obtained by the reaction of anhydrous glucose with 4-biphenylamine in 96% alcohol.

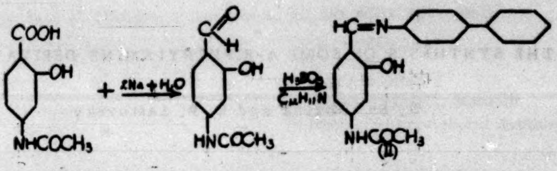


(I)

The glucoside of 4-biphenylamine reduces Fehling solution and is easily decomposed by 5% hydrochloric acid solution, which is evidence that the obtained glucoside is a glucosylarylamine, and not the azomethine.

The best results as regards both the quality and yield of the glucoside were obtained when the synthesis was run with freshly distilled 4-biphenylamine in anhydrous alcohol medium; the use of 96% alcohol is also permissible. Further reduction in alcohol concentration leads to oxidation of the 4-biphenylamine and hydrolysis of the already formed glucoside.

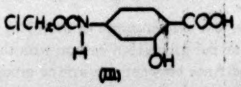
As is known, amines react readily with the acid chlorides of carboxylic acids. It seemed expedient to effect condensation between 4-niphenylamine and 4-aminosalicylic acid through the acid chloride of the latter. To protect its amino group the 4-aminosalicylic acid was acetylated. However, we were unable to obtain the acid chloride of 4-acetamidosalicylic acid; so we chose a different synthesis path, by analogy with the already described reaction of p-toluidine with salicylaldehyde, obtained by the reduction of salicylic acid, with the formation of N-salicylidene-p-toluidine [7]. To avoid secondary processes the synthesis was not run with 4-aminosalicylic acid, but instead was run with its acetyl derivative:



(II)

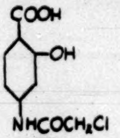
Repetition of the conditions for the synthesis of N-salicylidene-p-toluidine failed to give a positive result. Raising the temperature from 20 to 50-55°, increasing the time of adding the metallic sodium, and introducing additional holding at 50°, all had a favorable influence on the process. 4-(4-Acetamidosalicylidene)aminobiphenyl (II) was obtained for the first time.

To determine the influence of the carboxyl group in compounds of this type on the antitubercular activity, it appeared of interest to condense 4-niphenylamine with 4-aminosalicylic acid to at the amino group. Attempts to effect direct condensation of the indicated compounds failed to give positive results; consequently, the previously unknown 4-(chloroacetamido)salicylic acid (III) was first prepared.

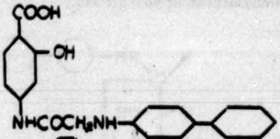


(III)

The condensation of 4-(chloroacetamido)salicylic acid with 4-biphenylamine was run in 96% ethyl alcohol and led to the previously unknown 4-[2-(4-biphenylamino)acetamido]salicylic acid (IV):



(III)



(IV)

The same as for the synthesis of the glucoside of 4-biphenylamine, both the degree of purity of the 4-biphenylamine and the alcohol concentration show decisive influence on the condensation reaction.

The compounds synthesized by us showed in vitro tuberculostatic activity; however, the data were not supported in the experiments with mice.

EXPERIMENTAL

4-Biphenylamine Glucoside. A mixture of 33.8 g (0.2 mole) of 4-biphenylamine, freshly distilled at 8-10 mm and having freezing point 52.5-53°, and 4 g of anhydrous glucose was dissolved at 50-60° in 200 ml of 96% alcohol. To this solution was added 4 g of activated wood charcoal, and after heating for 15 minutes under reflux the charcoal was filtered. To the filtrate was added 32 g of glucose (a total of 36 g or 0.2 mole), and with periodic stirring the solution was heated on the boiling water bath for 6 hours. After a second treatment with charcoal the clear colorless solution was let stand for two days to crystallize. The 4-biphenylamine glucoside crystallized in the form of needles, at times as clumps; it was filtered, washed with alcohol and ether, and dried in a desiccator over calcium chloride. Yield 52-53 g (70-80%). M. p. 111-112° (decompn.). Readily soluble in alcohol and benzene, and insoluble in ether.

If the 4-biphenylamine glucoside is obtained with a lower melting point, then it is treated several times with ether (to remove slight traces of unreacted 4-biphenylamine) and recrystallized from alcohol.

3.270 mg sub.: 0.123 ml N_2 (24°, 750 mm). 4.360 mg sub.: 0.163 ml N_2 (23°, 750 mm). 4.718 mg sub.: 11.284 mg CO_2; 2.665 mg H_2O. 5.907 mg sub.: 14.158 mg CO_2; 3.315 mg H_2O. Found %: C 65.26, 65.41; H 6.32, 6.28. N 4.27, 4.26. $C_{18}H_{21}O_5N$. Calculated %: C 65.26; H 6.40; N 4.24.

4-(4-Acetamidosalicylidene)aminobiphenyl. In a three-necked flask, fitted with stirrer, was placed 900 ml of 0.6% sodium carbonate solution and 17.85 g (0.092 mole) of 4-acetamidosalicylic acid. To this solution of sodium 4-acetamidosalicylate was added at 80° 24.0 g (0.142 mole) of freshly distilled 4-biphenylamine; then with good (and careful) stirring at 50-55° was added 225 g of sodium chloride and in the course of two hours 370 g of 2% sodium amalgam and 120 g of boric acid, making sure that the reaction always remained acid to litmus. After all of the sodium amalgam had been added, the mass was stirred for another 2 hours at 50-55°. The resulting azomethine was separated, washed with cold water, and dried at 40-45°. For purification the azomethine was treated 3-4 times with ether, and then recrystallized from alcohol. Yield 14.0-14.5 g (46.5-47.0%), based on 4-acetamidosalicylic acid. M. p. 233-234°.

4.215 mg sub.: 0.323 ml N_2 (25°, 735 mm). 5.045 mg sub.: 0.388 ml N_2 (25°, 747 mm). Found %: N 8.64, 8.66. $C_{21}H_{18}O_2N_2$. Calculated %: N 8.48.

Spectral analysis showed the absence of mercury in the compound.

4-[2-(4-biphenylamino)acetamido]salicylic acid. In a round-bottomed flask, fitted with reflux condenser, was placed 300 ml of alcohol, 17.3 g (0.075 mole) of 4-(2-chloroacetamido)-salicylic acid with m. p. 235-236°, and 25.5 g (0.15 mole) of freshly distilled 4-biphenylamine. After heating for 10-15 minutes the obtained solution was treated with charcoal, and the filtrate was boiled for 7 hours. The resulting 4-[2-(4-biphenylamino)acetamido] salicylic acid was filtered, washed with hot alcohol, and dried at 60-70°.

4-[2-(4-Biphenylamino)acetamido]salicylic acid is insoluble in benzene, toluene, xylene, chloroform, carbon tetrachloride, alcohol and ether. We were unable to recrystallize it. It was purified from impurities by successive boiling under stirring with benzene, alcohol, and ether. Yield 12 g (44.5%). M. p. 231;5-232.0°.

3.410 mg sub.: 0.233 ml N_2 (22°, 745 mm). 4.725 mg sub.: 0.320 ml N_2 (23°, 719 mm). 0.5373 g sub.: 14.82 ml 0.1 N NaOH. 0.5120 g sub.: 14.08 ml 0.1 N NaOH. Found %: N 7.75, 7.67. M 362.6, 361.6. $C_{21}H_{18}O_4N_2$. Calculated %: N 7.74. M 362.6.

4-Acetamidosalicylic Acid. A solution of 87.5 g (0.5 mole) of sodium 4-aminosalicylate in 450 ml of water was prepared. To the filtered solution was added with vigorous stirring at 30° 60.6 g (0.6 mole) of acetic anhydride and the mixture stirred for another 5 hours. Yield 73.7 g (75.6%). After recrystallization from 35% alcohol (1:20), m. p. 225-226°.

5.940 mg sub.: 0.352 ml N_2 (22°, 740 mm). 5.730 mg sub.: 0.336 ml N_2 (22°, 740 mm). Found %: N 7.26, 7.20. $C_9H_9O_4N$. Calculated %: N 7.18.

4-(2-Chloroacetamido)salicylic Acid. To a solution of 25 g (0.14 mole) of sodium 4-aminosalicylate in 280 ml of water was added 32 g of sodium bicarbonate at 35-40°. After the latter had dissolved the mass was cooled to 20° and 32 g (0.283 mole) of chloroacetyl chloride was added from a dropping funnel over a period of 10-15 minutes. The mass was stirred for 1 hour, and the resulting 4-(2-chloroacetamido)salicylic acid was filtered, washed with water, and dried at 50-60°. Yield 22-23 g (69.5-72.0%), m. p. 235-236°.

4.665 mg sub.: 0.252 ml N_2 (21°, 750 mm). $C_9H_8O_4ClN$. 0.1860 g sub.: 8.2 ml 0.1 N $AgNO_3$. 0.2100 g sub.: 9.1 ml 0.1 N $AgNO_3$. 0.2186 mg sub.: 9.5 ml 0.1 N NaOH. 0.1790 mg sub.: 7.9 ml 0.1 N NaOH. Found %: N 6.19; Cl 15.2, 15.6. M 229.5, 226.6. $C_9H_8O_4ClN$. Calculated %: N 6.10; Cl 15.5. M 229.5.

SUMMARY

1. Some previously unknown derivatives of 4-biphenylamine were obtained and characterized.

2. A method was developed for the preparation of the glucoside of 4-biphenylamine.

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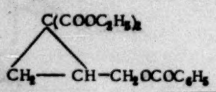
REACTION OF DIBROMOALLYL ALCOHOL WITH DISODIOMALONIC ESTER

V. D. Yasnopolsky

The Perkin reaction of dihalo derivatives of open chain hydrocarbons, in which the halogens are found on different carbon atoms, with disodiomalonic ester leads to the formation of cyclic acid esters. In developing these syntheses it appeared of interest to introduce into the reaction such substances as had a group with an active hydrogen atom in the α-position to one of the halogen-containing carbons. Dibromoallyl alcohol was taken in the present work and its behavior toward disodiomalonic ester was studied.

Experiment revealed that in the reaction of dibromoallyl alcohol with disodiomalonic ester 62% of the dibromoallyl alcohol is recovered unchanged, while the remainder is consumed in the formation of a brown resin.

The benzoate of dibromoallyl alcohol reacted smoothly with disodiomalonic ester to give the crystalline ester of 1-hydroxymethyl-2,2-cyclopropanedicarboxylic acid:



Since the Conrad and Perkin syntheses with malonic ester are usually run in anhydrous alcohol, it then follows that the presence of substances with a hydroxyl group in the reaction medium during the time of running such a synthesis will fail to show a negative influence on the reaction course. Consequently, the peculiar behavior shown by dibromoallyl alcohol in the given synthesis should be explained as being exclusively due to the hindering action of the hydroxyl group in its α-position to one of the halogen-containing carbon atoms on the properties of the dibromide.

EXPERIMENTAL

Bromination of Allyl Alcohol. To 58 g of allyl alcohol with ice cooling was added in drops 160 g of bromide. The reaction product was distilled. After removing several grams of unreacted allyl alcohol the dibromoallyl alcohol distilled at 205.5-206°. According to Lespieau [1]: b. p. 205-208°. Since Lespieau fails to show other constants, then d_4^{20} 1.8960, n_D^{20} 1.5360 were determined.

Preparation of Disodiamalonic Ester. To 17 g of sodium, cut into small pieces and found under a layer of dry benzene, was added 55 g of malonic ester. Instantly the evolution of hydrogen bubbles began. The reaction mixture was let stand a day. The resulting salve like mass still contained some small pieces of sodium and was heated on the water bath until a yellow solution was obtained.

Preparation of the Benzoate of Dibromoallyl Alcohol and Its Reaction with Disodiomalonic Ester. A survey of the literature revealed that this ester was still unknown. The ester was prepared by the Schotten-Baumann reaction. To 25 g of dibromoallyl alcohol was added 16 g of benzoyl chloride and to the emulsion of these two substances was added 10 ml of 50% sodium hydroxide solution. The mixture was vigorously shaken for about 1 hour, and then allowed to stand overnight. A precipitate in the form of tiny needles was obtained, which were separated from the liquid, washed with water, and air-dried. Yield 4 g (10.8%). The crystals are poorly soluble in cold benzene and readily soluble in hot benzene. After two recrystallizations from benzene the crystals had m. p. 86-88°.

To a benzene solution of disodiomalonic ester, prepared from 8 g of malonic ester and 2.5 g of metallic sodium, was added 15 g of the benzoate of dibromoallyl alcohol. The mixture was heated on the water bath for 5 hours. After cooling the solution the liquid was filtered from the precipitate and poured into a crystallizing dish. Removal of the benzene by evaporation left needlelike crystals. Two recrystallizations from benzene gave 7.5 g of crystals as coarse needles with m. p. 115-117°.

0.0206 g sub.: 0.0477 g CO_2; 0.0111 g H_2O. 0.1310 g sub.: 21.15 g benzene: Δt 0.174°. Found %: C 63.22; H 6.00. M 321.6. $C_{17}H_{20}O_6$. Calculated %: C 63.76; H 6.26. M 321.6.

SUMMARY

The reaction of the benzoate of dibromoallyl alcohol with disodiomalonic ester gave the ester of 1-hydroxymethyl-2,2-cyclopropanedicarboxylic acid.

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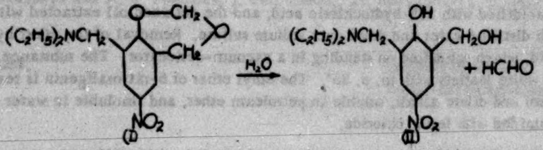
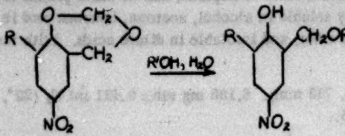
THE SYNTHESIS OF 5-NITROSALIGENIN AND ITS ETHERS

V. I. Stavrovskaya

In elucidating the structure of 3-diethylaminomethyl-5-nitrosaligenin methylene ether (I), described by Einhorn [1] as "2-hydroxy-5-nitrobenzyldiethylamine", it was shown by us that the heating of this substance with dilute sulfuric acid leads to the evolution of formaldehyde and the formation of a new compound [2]. Further study established that this new compound is 3-diethylaminomethyl-5-nitrosaligenin (II), the formation of which proceeds in accord with the following scheme:



The use of this method for the synthesis of 5-nitrosaligenin from 5-nitrosaligenin methylene ether led, under prolonged heating, to the formation of a pliant mass instead of the desired 5-nitrosaligenin. With short heating the original product was recovered unchanged. We were of the opinion that the negative results of the last reaction was associated with the insolubility of the 5-nitrosaligenin methylene ether in dilute sulfuric acid. Actually, the addition of alcohol as a solvent led to ring opening, but together with this, also to etherification of the formed 5-nitrosaligenin. With this method the previously unknown methyl and ethyl ethers of 5-nitrosaligenin and the methyl ether of 3-diethylaminomethyl-5-nitrosaligenin were synthesized.



where R = H, $(C_2H_5)_2NCH_2$; R' = CH_3, C_2H_5.

Prolonged boiling of the 5-nitrosaligenin methylene ether with 10% sodium hydroxide solution also caused ring rupture, and here we isolated 5-nitrosaligenin as the reaction product. However, in this case the reaction proceeds with poor yield.

The above described reactions can serve as a method for the synthesis of substituted saligenin derivatives and their ethers.

EXPERIMENT

3-Diethylaminomethyl-5-nitrosaligenin. 3-Diethylaminomethyl-5-nitrosaligenin methylene ether (2 g) was boiled with dilute sulfuric acid (5 ml, 1 : 1 by volume) for an hour; here the strong odor of formaldehyde was noted. The clear liquid after cooling was diluted with water (20 ml), made alkaline with 10% sodium hydroxide solution, and filtered from undissolved particles. The filtrate was acidified with hydrochloric acid until it showed acid to Congo and then it was saturated with potash until a yellow solid separated. The precipitate was filtered (1.2 g), recrystallized from water, and then from benzene. Fine bright yellow needles; m. p. 81-82°.

3-Diethylaminomethyl-5-nitrosaligenin is readily soluble in alcohol, and soluble in benzene, water, and in dilute acids and alkalies. With ferric chloride it gives a cherry-red color.

3.813 mg sub.: 0.382 ml N_2 (20°, 739 mm). 2.940 mg sub.: 0.294 ml N_2 (21°, 739 mm). Found %: N 11.35, 11.29. $C_{12}H_{18}O_4N_2$. Calculated %: N 11.02.

The hydrochloride is white. It can be recrystallized from either alcohol or 10% hydrochloric acid. M. p. 166-167° (decompn).

4.208 mg sub.: 0.372 ml N_2 (21°, 747 mm). 4.245 mg sub.: 0.363 ml N_2 (22°, 750 mm). Found %: N 10.09, 9.76. $C_{12}H_{19}O_4N_2Cl$. Calculated %: N 9.64.

5-Nitrosaligenin Ethyl Ether. In a small flask, fitted with reflux condenser, was placed 5-nitrosaligenin methylene ether (3 g), ethyl alcohol (15 ml) and concentrated sulfuric acid (2.5 ml). The solution was boiled for 6 hours, after which water was added (50 ml), and the yellow liquid separating on the bottom of the flask was extracted with ether. The ether solution was washed with distilled water and dried over sodium sulfate. Distilling off the ether gave a residue of 1.9 g of yellow mobile liquid, which was dissolved in 5% sodium hydroxide solution, filtered from a small amount of flock, acidified with 10% hydrochloric acid, and the obtained oil extracted with ether. The ether solution was washed with distilled water and dried over sodium sulfate. Removal of the ether by distillation left 1.4 g of viscous yellow liquid, which solidified on standing in a vacuum-desiccator. The substance was recrystallized from petroleum ether to give white leaflets with m. p. 85°. The ethyl ether of 5-nitrosaligenin is readily soluble in ether, benzene, acetone, alcohol and dilute alkali, soluble in petroleum ether, and insoluble in water and dilute acids. A cherry-brown color is obtained with ferric chloride.

4.412 mg sub.: 0.284 ml N_2 (28°, 734 mm). 4.746 mg sub.: 0.304 ml N_2 (28°, 739 mm). Found %: N 7.04, 7.16. $C_9H_{11}O_4N$. Calculated %: N 7.11.

5-Nitrosaligenin Methyl Ether. 5-Nitrosaligenin methylene ether (3 g), methyl alcohol (15 ml) and concentrated sulfuric acid were heated in a small flask under reflux, with boiling of the liquid inside the flask. The flask contents failed to go into solution after heating for 3 hours., consequently there were added alcohol (10 ml), sulfuric acid (2 ml) and water (0.5 ml). The heating was continued for another 12 hours, after which the reaction liquid was a clear yellow solution to which after cooling, water was added (50 ml). Further treatment was the same as for the preparation of the ethyl ether. The yield of yellowish liquid was 2.7 g, which quickly solidified. The substance crystallizes as plates from either petroleum ether or heptane, and as white prisms from water. M. p. 109°. The methyl ether of 5-nitrosaligenin is very soluble in alcohol, acetone, benzene and in dilute alkalies, soluble in heptane and water, poorly soluble in petroleum ether, and insoluble in dilute acids. With ferric chloride it gives a cherry-red color.

5.984 mg sub.: 0.421 ml N_2 (25°, 733 mm). 6.135 mg sub.: 0.431 ml N_2 (22°, 728 mm). Found %: N 7.77, 7.79. $C_8H_9O_4N$. Calculated %: N 7.65.

3-Diethylaminomethyl-5-nitrosaligenin Methyl Ether. 3-Diethylaminomethyl-5-nitrosaligenin- methylene ether (2 g), methyl alcohol (10 ml), concentrated sulfuric acid (6 ml) and water (0.5 ml) were boiled for 8 hours. To the flask after cooling was added water (20 ml), and then 10% sodium hydroxide solution to alkaline reaction. The solution was filtered, acidified with 10% hydrochloric acid, and saturated with potash. The resulting yellow oil was extracted with ether. The ether solution was dried over sodium sulfate. Removal of the ether by distillation left 1.2 g of thick yellow liquid, which was dissolved with heating in a very small amount of water. Yellow needles separated on cooling. M. p. 80.5-82°.

The methyl ether of 3-diethylaminomethyl-5-nitrosaligenin is readily soluble in ether, water, benzene, and in dilute alkalies and acids, and poorly soluble in petroleum ether. With ferric chloride it gives a cherry-red color.

5.962 mg sub.: 0.558 ml N_2 (23°, 745 mm). 5.801 mg sub.: 0.549 ml N_2 (23°, 746 mm). Found %: N 10.58, 10.71. $C_{12}H_{18}O_4N_2$. Calculated %: N 10.45.

5-Nitrosaligenin. 5-Nitrosaligenin methylene ether (1.5 g) was boiled in 10% sodium hydroxide solution (20 ml) for 5 hours. The yellow solution after cooling was filtered from the solid (1.2 g), acidified with 10% hydrochloric acid until acid to Congo, and extracted with ether. The ether solution was dried over sodium sulfate. Removal of the ether by distillation left 0.3 g of mobile yellow liquid, which congealed on rubbing and became solid when petroleum ether was added. The substance was filtered (0.2 g) and recrystallized from benzene. Yellow needles, m. p. 125° (the literature gives m. p. 126° [1]).

5-Nitrosaligenin is readily soluble in alcohol, ether and acetone, soluble in benzene and water, poorly soluble in petroleum ether, and soluble in dilute acids and alkalies. With ferric chloride it gives a red color.

Found %: N 8.63, 8.49. $C_7H_7O_4N$. Calculated %: N 8.28.

The solid product, failing to dissolve when boiled with alkali, burns, but does not melt. Its structure was not established.

SUMMARY

1. A method for the synthesis of substituted derivatives of saligenin and its ether was described.

2. The methyl and ethyl ethers of 5-nitrosaligenin, 3-diethylaminomethyl-5-nitrosaligenin, and its methyl ether, were synthesized and characterized.

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* T. p. = C. B. Translation pagination.

5-Nitroeugenol is readily soluble in alcohol, ether and acetone, [illegible] in benzene and water, [illegible] in petroleum ether, and soluble in alkali [illegible]. With [illegible] it gives a [illegible].

Found %: N 6.82, 6.84. $C_{10}H_{11}O_4N$. Calculated %: N 6.70.

2. The solid product [illegible] in alcohol was [illegible] but its structure was not established.

SUMMARY

1. A method for the synthesis of substituted derivatives of [illegible] was described.

2. The methyl and ethyl ethers of 5-nitroeugenol, [illegible], were synthesized and characterized.

LITERATURE CITED

[1] [illegible]

[2] [illegible]

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[illegible]

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* See C. B. Translation pagination.

CHITIN

II. GLYCEROL ETHERS OF CHITIN

S. N. Danilov and E. A. Plisko

The synthesis of esters and ethers proceeds with considerably more difficulty for chitin than it does for cellulose, which it is impossible not to associate with the low degree of swelling shown by chitin in acids and especially in alkalies [1].

Information on the esters of chitin was to a large degree summarized in the studies of P. P. Shorygin and his coworkers [2-4]. They indicate that the acetylation [3] and nitration [2] conditions, used with success in the case of cellulose, proved to be unsuitable for chitin, so that it became necessary to select more suitable acetylating and nitrating mixtures, running the reaction for many hours.

The indicated studies also contain a description [4] of the ethers (methyl) and chitin. The methylation of chitin with dimethyl sulfate in the presence of sodium hydroxide proceeds slowly and incompletely. After 45-fold methylation a chitin methyl ether with 9.34% of methoxyl groups (degree of substitution about 0.7 hydroxyl) was obtained. The reason for the difficult methylation of chitin should be sought in its weak swelling in alkali.

By using the technique of preliminary treatment of the chitin with hydrochloric acid, which causes marked swelling of the chitin, or with concentrated caustic solution, the indicated authors obtained chitin as a mass, readily crushed into a powder. In this case after 15 methylations a chitin methyl ether containing 16.07% methoxyl groups (substitution about 1.1 hydroxyls) was obtained.

The obtained chitin monomethyl ether was soluble in formic acid, and showed strong swelling in glacial acetic acid.

Later, it was briefly mentioned in other studies [5] that the reaction of alkali chitin with dimethyl sulfate yields methylchitin, soluble in cold and insoluble in hot water, similar to methylcellulose and hydroxybutylcellulose [6]; here it was indicated that chitin forms ethers (hydroxyethyl) with ethylene chlorohydrin and ethylene oxide, but neither the synthesis conditions nor the properties of the ethers themselves were given.

The purpose of our studies was to specifically obtain the unknown water-soluble (hydrophilic) ethers of chitin – the hydroxyethyl and glycerol ethers of different degrees of substitution, which fact would be of interest for rendering chitin soluble in aqueous media [7].

The glycerol ethers of chitin are described in our above mentioned communication. Such ethers for cellulose were synthesized by Shorygin [8] and Danilov [9], together with their coworkers, as linear and three-dimensional molecules. The reaction of alkali chitin with glycerol monochlorohydrin and glycidic alcohol was used to synthesize the glycerol ethers of chitin.

The synthesis proceeded well, provided well pulverized chitin was used, which had first been precipitated from solution in 78.4% phosphoric acid, or if the chitin in the caustic was cooled at –40 to –70°, or if the impregnation with the caustic was run for several hours under reduced pressure, with an etherification time of 30-40 hours, and a temperature of about 60°. The higher degrees of substitution (around 1-1.6 hydroxyl groups) were predominantly obtained under repeated etherification. In not a single case were the ethers soluble in water, in contrast to the corresponding cellulose ethers; some of the specimens either partially or completely dissolved in 4 and 8% sodium hydroxide solution, and in 3-50% acetic acid. All of the glycerol ether specimens were soluble in dilute mineral acids, which, apparently, was facilitated by the appearance of deacetylated amino groups.

The properties of the ethers, obtained through the monochlorohydrin, differ from the properties of the ethers obtained through the use of glycidic alcohol, and specifically in their lower degree of swelling or complete absence of swelling in dilute sodium hydroxide, in organic acids, and in water. Evidently, here there was a certain "stitching together" of the molecules due to the presence of trace impurities of glycerol dichlorohydrin in the glycerol monochlorohydrin, which impurities we were unable to remove under our distillation conditions.

A characteristic of chitin etherification is the strongly defined heterogeneity of the reaction products, which is also characteristic of the cellulose ethers, but to a lesser degree. The ethers based on the glycidic alcohol are especially heterogeneous, in addition to which the glycidic alcohol suffers considerably self-condensation under the synthesis conditions.

Determination of the composition of the chitin glycerol ethers is complicated by the fact that in their synthesis a partial deacetylation of the amino groups is observed, as can be seen when the percentage amounts of nitrogen, acetyl and glycerol groups in the obtained ethers are compared. The general composition of the obtained glycerol ethers of chitin is expressed by the formula:

$$[C_6H_7O_2(NHCOCH_3)_y(NH_2)_{1-y}(OH)_{2-x}(OCH_2CHOHCH_2OH)_x]_n$$

$$\text{or } [C_6H_9O_4(NHCOCH_3)_y(NH_2)_{1-y}(> CHCHOHCH_2OH)_x]_n$$

where the highest value of $\underline{x}$ was 1.6, while $\underline{y}$ varied in the limits 0.3-0.6 of the original value. For some of the glycerol ethers the characteristic viscosities in 4 and 8% caustic solutions were determined, in numerical value proving to be close to those obtained for solutions of chitin itself, but in phosphoric acid.

EXPERIMENTAL

1. Chitin Glycerol Ethers Based on Glycerol Monochlorohydrin

The monochlorohydrin needed for the syntheses was prepared from glycerol in the usual manner, was repeatedly distilled to free it of the dichlorohydrin, and had the following constants:

B. p. 110° (8 mm), n_D^{20} 1.4789, d_4^{20} 1.3214, MR_D 23.89; calc. 23.97.

In some of the synthesis experiments the chitin specimens used had been obtained by precipitation from solutions in 78.4% phosphoric acid, but for Specimen 1 a low degree of etherification (6.14% of glycerol groups) was obtained under the conditions described below.

A favorable influence for reaction to proceed is shown by the gringing of the chitin and especially by the repeated freezing and thawing of the caustic used in the swelling of the chitin.

We will describe one of the experiments on the synthesis of the ether in which glycerol monochlorohydrin was used as the etherification agent.

Six grams of dry chitin was covered with 90 ml of 30% sodium hydroxide solution in a small flask (100 ml), which was then tightly closed and placed in a Dewar vessel containing solid carbon dioxide, where alternate freezing (for 30 minutes) and thawing (for 60 minutes) was repeated 5 times in a time interval of 7.5 hours. The caustic was squeezed out from the strongly swollen chitin to a 3-fold weight. The resulting alkali chitin cake was ground in a porcelain mortar and then placed in a reaction flask, fitted with stirrer, where the monochlorohydrin (15 g) in acetone (100 ml) was introduced in a 4 : 1 ratio of monochlorohydrin to chitin. The flask was heated on the water bath (60°) for 40 hours (with interruptions). The control used to determine the end of synthesis was a negative Beilstein test for chlorine in the organic substance.

The preparation, filtered from the acetone, was introduced into water, where the alkali was neutralized with acetic acid, after which the product was washed and dried. Yield 5.8 g. The substance (Specimen 1) fails to swell in water and in 4% sodium hydroxide solution, but does show some swelling in 8% sodium hydroxide solution and in concentrated formic acid, and is soluble in 60% sulfuric acid, in concentrated hydrochloric acid (d 1.12) and in 78-97% phosphoric acid, which indicates the linear nature of the molecules in the substance.

A part of the obtained ether specimen (3 g) was etherified a second time under the same conditions and same ratio of substances as in the previous synthesis. After a second etherification the behavior of Specimen 1_1 toward solvents failed to change, although the degree of substitution was raised: %$OCH_2CHOHCH_2OH$ for Specimen 1 was 25.66, while for Specimen 1_1 it was 32.32. We will mention that a high degree of substitution was also achieved in that modification of the synthesis where the thoroughly pulverized chitin (0.25 mm screen) was made to swell in 43% sodium hydroxide under good vacuum for 5-10 hours, and where 300 ml of sodium hydroxide solution was taken for 20 g of chitin. The alkali chitin, squeezed to a 2.8-fold weight, was heated at 60° for 40 hours with glycerol monohydrin in acetone.

A part of the obtained Specimen 2 was subjected to a second treatment by the just given directions, beginning with the steeping of the prepared ether in the caustic. The same treatments were successively repeated a third and fourth time. In this manner Specimens 2, 2_1, 2_2 and 2_3 were obtained, in which the degree of substitution (percent of glycerol residues) gradually rose.

When compared with Specimen 2, the behavior of the obtained specimens (2_1, 2_2 and 2_3) toward water and other solvents was impaired. Thus, Specimen 2_2 was partially soluble in diluted acids — sulfuric (60%), concentrated hydrochloric and phosphoric (50-97%), while Specimen 2_3 was already insoluble in them, and proved to be completely nonswelling in alkalies. With repitition of the synthesis it can be seen that the number of "stitches" increased due to the presence of dichlorohydrin impurities. A positive influence on the solubility of the specimens, especially in acids, could have been exerted by the fact that in the repeated syntheses the number of free amino groups (deacetylated by the alkali) increased, but this failed to be shown.

TABLE 1

Specimen Nos.	% Glycerol Residues	% Acetyl Groups	%C	%H	%N
2	23.77	–	–	–	–
2_1	32.37	8.36	–	–	–
2_2	47.40	–	–	–	–
2_3	49.00	3.70	47.40	7.88	3.63

Analysis of the specimens revealed that the degree of etherification gradually increased from Specimen 2 to Specimen 2_3, as can be seen from Table 1.

Specimen 2_3, on the basis of its complete analysis, can be assigned the structure:

$$C_{11}H_{20.0}O_{7.25}N_{0.75}$$

or

$$[C_6H_7O_2(NHCOCH_3)_{0.25}(NH_2)_{0.5}(OH)_{0.5}(OCH_2CHOHCH_2OH)_{1.5}]_n.$$

2. Chitin Glycerol Ethers Based on Glycidic Alcohol

Glycidic alcohol was obtained from the monochlorohydrin in known manner [10] (in yields up to 70% when the amount of metallic sodium was increased) and had the following constants:

B. p. 56-57° (1-1.5 mm), n_D^{20} 1.4336, d_4^{20} 1.1370, MR_D 16.90; calc. 17.15.

Alkali chitin was prepared by soaking chitin in 30-43% sodium hydroxide solution at room temperature in vacuo for 12 hours, or the method of repeated alternate freezing and thawing of the caustic solution containing the pulverized chitin was used. The coefficient of squeezing was 3. The synthesis was run in the same manner as when the monochlorohydrin was used. Usually the synthesis conditions were: 4 : 1 molar ratio of glycidic alcohol to chitin, temperature 56°, time 12-30 hours, and in either acetone medium or without it.

The glycerol ethers of chitin, obtained using glycidic alcohol, always showed swelling in moderately and strongly diluted, acetic, formic, oxalic and levulinic acids, and even dissolved in them, not to mention the mineral acids, which are excellent solvents; at times they dissolved in 4 and 8% sodium hydroxide solution and even partially in water. For this reason it was necessary to remove the alkali, not by the usual washing with water, but by dialysis and electrodialysis, in which connection cellophane was used as the membrane.

The demineralized moist product, swollen in water and partially dissolved in it, was precipitated by the addition of acetone with constant stirring. Here a white, highly swollen precipitate was obtained as a friable clod. The substance was repeatedly treated with dry acetone, then with ethyl ether, and dried in a vacuum-oven without heat.

The moist white product was soft and slightly gummy, but after drying it could easily be ground to a powder in a mortar. The specimens, dried without heat, dissolved in 4-8% sodium hydroxide and in 3-50% acetic acid, showed strong swelling in water, glacial acetic acid, and in dilute and concentrated formic and levulinic acids, but in the case of overdrying they showed considerably poorer swelling. For the case of glycidic alcohol the syntheses gave specimens with a moderate amount of glycerol residues, ranging from 6 to 36.70%. A higher degree of etherification was achieved by making a second addition of the glycidic alcohol in the ratio of 4 moles of the alcohol to 1 mole of chitin. The total yields of the products reached 110% of the original chitin weight.

A comparison of the nitrogen and acetyl group analyses shows that there is considerable deacetylation of the amino groups under the influence of the alkali. From either the reaction mass or from the isolated product fractions could be obtained that differed in their solubility in both alkali and in 3-50% acetic acid.

The analyses for some of the obtained specimens are given in Table 2.

TABLE 2

Specimen Nos.	Synthesis conditions	Elementary composition (in %) C	H	N	% Acetyl Groups CH_3CO	% Glycerol Residues $OCH_2CHOHCH_2OH$
3	Steeping of chitin in 43% alkali solution in vacuo. The glycidic alcohol was added three times in amounts of 4 moles, without adding alkali; the synthesis was run for 12 hours in acetone medium	46.20	7.43	4.81	4.67	42.45
4	The same as for Specimen 3, but the synthesis was run in acetone medium					
	Fraction 1	45.56	7.16	6.74	–	14.45
	Fraction 2	45.33	7.73	4.35	–	22.60
4_1	Before its isolation Specimen 4 was additionally treated with 4 moles of glycidic alcohol, 12 hours, 56°, in acetone	45.97	7.31	4.88	–	36.70

Both the preceding chitin glycerol ether specimens and the specimens based on glycidic alcohol were analyzed for their nitrogen content by the Dumas and Kjeldahl methods, in known manner [11] for the number of acetyl groups, while the number of glycerol radicals was determined by the Zeisel method. In all cases the average values of 2-3 parallel determinations are given.

Such glycerol ether specimens, even those with a low degree of substitution (with a glycerol radical content of 8.13, 13.25, 5.98 and 5.44%), showed swelling in glacial and 50% acetic acid, in different concentrations of formic acid, and dissolved in mineral acids. With a higher degree of etherification the specimens showed swelling in 4-8% sodium hydroxide and even in water, and became soluble in very dilute organic acids, which is characteristic for Specimens 3 and 4 (Table 2).

The composition for Specimens 3 can be shown by the formula.

$$C_{10.3}H_{18.9}O_{6.8}N_{0.9}$$

or

$$[C_6H_7O_2(NHCOCH_3)_{0.29}(NH_2)_{0.63}(OH)_{0.76}(OCH_2CHOHCH_2OH)_{1.24}]_n.$$

The glycerol ethers of chitin, dissolving in 4 and 8% sodium hydroxide, were characterized by their viscosities at 5 concentrations, ranging from 0.05 to 0.79 g/100 ml at 20 ± 0.01°. For Specimen 4 the characteristic viscosities were found to be, in 4% sodium hydroxide – 2.6, and in 8% sodium hydroxide – 2.4; for Specimen 4_1, Fraction 2, the corresponding values were 3.9 and 2.9. The proximity of the values of the characteristic viscosities for Specimens 4 and 4_1, combined with the proximity of their composition, speaks in favor of their molecular weights being close.

Although the chitin glycerol ethers, obtained through the glycidic alcohol, show considerable solubility, still the products of the syntheses are heterogeneous; we were unable to obtain specimens that were completely soluble in water or even in dilute caustic solution. In synthesizing the ethers considerable self-condensation of the glycidic alcohol under the influence of alkali and heat is observed.

SUMMARY

1. Glycerol ethers of chitin have been synthesized for the first time by the reaction of either glycerol monochlorohydrin or glycidic alcohol with chitin in the presence of alkali; deacetylation of the amino groups in chitin proceeds both during the time of preparing the chitin for reaction and in the synthesis itself.

2. The success of the synthesis depends on the use of thoroughly pulverized chitin and especially on the ability to achieve the highest possible degree of swelling in alkali by either the technique of repeated alternate freezing and thawing of the alkali solutions containing the chitin, or by the method of steeping the chiting under reduced pressure at room temperature.

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CHEMISTRY OF CHLOROMYCETIN (LEVOMYCETIN)

V. RACEMIZATION OF L-THREO-1-(p-NITROPHENYL)-2-(DICHLOROACETAMIDO)-1,3-PROPANEDIOL WITH SUBSEQUENT CONVERSION OF THE RACEMATE INTO CHLOROMYCETIN (LEVOMYCETIN) [1]

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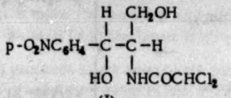
The chloromycetin molecule (levomycetin, chloroamphenicol), being D-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (I), contains two asymmetric carbon atoms, as a result of which in the process of synthesizing this compound there can be formed, together with it,



$$p\text{-}O_2NC_6H_4-\overset{\displaystyle H}{\underset{\displaystyle HO}{C}}-\overset{\displaystyle CH_2OH}{\underset{\displaystyle NHCOCHCl_2}{C}}-H$$

(I)

all three of its theoretically possible spatial isomers: L-threo-, D-erythro- and L-erythro-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediols. These three stereoisomers differ from chloromycetin in that for all practical purposes they are completely devoid of antibacterial, antirickettsial and antiviral activity, and in addition they show considerable toxicity. In connection with this, immediately after the structure and synthesis of chloromycetin had been elucidated, there arose two problems before the investigators: 1) to find rational methods for the separation of chloromycetin from its inactive and toxic stereoisomers, and 2) to elucidate the possibility of converting these stereoisomers into chloromycetin. The first of these problems was successfully solved by us as early as 1949 [2]; simultaneously and independent of our work the problem was solved by some American investigators, and later a number of methods were described in the literature for the separation of chloromycetin or its intermediate synthesis products from the corresponding compounds, possessing the D,L-erythro and L-threo configurations.* As regards the second problem, here until recently only a partial solution had been achieved — it was possible to realize only the isomerization of compounds of the erythro series into compounds of the threo series [3-5, 13, 14], while the question as to the possibility of racemizing compounds of the L-threo series remained unanswered. This question was recently solved by us, in which connection a brief summary of the performed work was published as a preliminary communication [15]. In this paper we describe the results of those investigations in more detail.

As is known [3, 4, 6-10], in the synthesis process for chloromycetin it is usually the intermediately formed D,L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol that is subjected to separation into its optically active forms, and much less frequently the N-dichloroacetyl derivative of this compound (racemate of chloromycetin), obtaining thus as nonutilizable secondary products the L-threo-aminodiol (II) or, correspondingly, the L-threo-N-dichloroacetamidodiol (III). In elucidating the possibility for the direct racemization of compounds (II) and (III), and also of the azomethine and N,N,O-, and N,O,O-acyl derivatives of the first of them,** all we obtained were negative results. In the treatment of all of these compounds with diverse acidic and basic substances, and also with many other reagents under various reaction medium and temperature conditions,* either racemization failed to proceed, or it was accompanied by very profound changes in the compounds being racemized. The difficultly for racemization of our investigated substances was, apparently, associated with the fact that in their molecules the groupings were absent, capable of essentially augmenting the mobility of the hydrogen atoms found at the asymmetric carbon atoms; consequently, it was decided to destroy one of the centers of asymmetry, at the same time creating a grouping that would facilitate racemization of the second center, and to combine the realization of the racemization process itself with the reduction of the first center of asymmetry. In accord with this we planned to convert the L-threo-aminodiol (II) into the L-threo isomer of chloromycetin (III), oxidize the secondary alcohol group in the latter to the carbonyl group, then subject the thus obtained optically active ketone (IV) to either sequential or simultaneous racemization and reduction, and finally end up with the racemate of chloromycetin (V).

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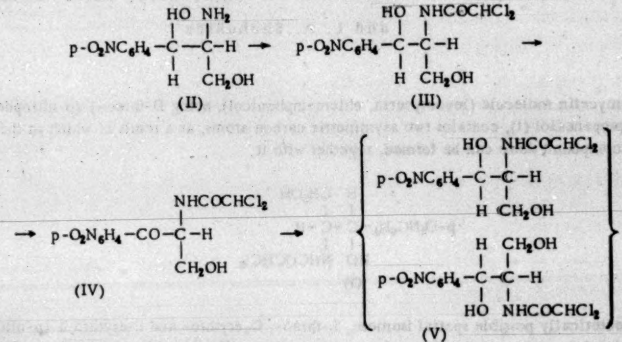
* For more details of this cf. [3], where a summary of the literature published up to 1953 is presented; for data on later investigations cf. [4-12].

** Containing, in part, strongly electron-accepting groups like, for example, the 2,4-dinitrobenzylidene or 2,4-dinitrobenzoyl radicals.



A detailed study of these reactions revealed that the given path permits easy passage from the L-threo compounds (II) and (III) to the racemate of chloromycetin (V), and then to chloromycetin (I) itself. The first step of our studied transformations – the N-dichloroacetylation of the L-threo-aminodiol (II) – was realized with the aid of the methyl ester of dichloroacetic acid, which ester acylates only the amino group in amino alcohols. It follows that this reaction should be run under the conditions developed by us earlier for the synthesis of chloromycetin [2, 16], taking the methyl dichloroacetate in not more than 20% excess and heating the reaction mixture at 90-100° for not over 30 minutes, so as to avoid reducing the yield and impairing the quality of the formed L-threo isomer of chloromycetin (III). It is also expedient to run this process in the presence of isoamyl alcohol, gradually distilling off the methyl alcohol formed in the reaction. The latter has to be removed due to the excellent solubility of the obtained L-threo compound (III) in it, while the presence of the isoamyl alcohol is desirable for the reason that it is a good solvent for the secondary reaction products. When the above indicated conditions are observed the yield of the L-threo compound (III) reaches 90-93%, in which connection the substance is obtained in such high purity that its purification by recrystallization is superfluous. However, it is even more convenient to run the reaction for the dichloroacetylation of the L-threo-aminodiol (II) in isopropyl alcohol medium at the boiling point of the latter, with subsequent dilution of the reaction mixture with water. By this method the L-threo compound (III) is obtained in the same yield and with the same purity as in the above described procedure.

It should be mentioned that the methyl dichloroacetate, needed for the synthesis of the chloromycetin (I) and its stereoisomer (III), can easily be obtained by the reduction of trichloroacetic acid with zinc dust in methyl alcohol medium, in which connection the esterification of the formed dichloroacetic acid can be achieved without its prior isolation by the method of boiling the reaction mixture with concentrated sulfuric acid. However, the dichloroacetic acid and its methyl ester, obtained both here and under the conditions described earlier in the literature [17], always contain small amounts of trichloroacetic and monochloroacetic acids or their esters, which cannot be completely removed by fractional distillation. The presence of these impurities even in traces sharply reduces both the quality and the yield of chloromycetin (I) and its stereoisomer (III).

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* For example, the inorganic and organic acids (H_2SO_4, HCl, HPO_3, HCOOH etc.), their anhydrides and acid halides ($SOCl_2$, SO_2Cl_2, $POCl_3$, PCl_5, Ac_2O, AcCl etc.), bases (pyridine, quinoline, piperidine, N-ethylpiperidine, etc., alkali carbonates and hydroxides, alcoholates (lithium, sodium, potassium, aluminum), and the alkali and alkaline earth metals (Li, Na, K, Mg, Ca) in the presence or in the absence of various polar and nonpolar solvents.

So as to render the methyl ester of dichloroacetic acid completely free of the methyl esters of trichloroacetic and monochloroacetic acids, it proved necessary to: 1) use a slight excess (0.1 mole) of zinc dust in the reduction, which permits achieving the complete absence of the methyl ester of trichloroacetic acid in the obtained products; 2) heat the obtained products with pyridine, which makes it possible to completely remove the methyl ester of monochloroacetic acid. Under the conditions developed by us a 50% yield of pure methyl dichloroacetate is obtained.

The second step of our proposed method for the racemization of the L-threo-aminodiol (II) – the oxidation of the L-threo-N-dichloroacetamidodiol (III) to the corresponding optically active ketone (IV) – can be realized with the aid of either chromic anhydride or potassium permanganate. In the attempts to find the optimum conditions for the oxidation of compound (III) with chromic anhydride the influence on the process of the medium (water, acetone, acetic acid, sulfuric acid), the amount of oxidizing agent used (from 0.5 to 2 moles), the time of its addition (from 1.5 to 5.5 hours), and the temperature (from 45 to 105°), was studied; here it was established that independent of the oxidation conditions a part of the original compound (III) always remains unchanged, while another part is subjected to deeper oxidation clear up to p-nitrobenzoic acid, as a result of which the ketone (IV) is formed in low yield.* In addition, the oxidation with chromic anhydride proceeds slowly and is accompanied by the formation of tarry products, which make the isolation and purification of the ketone (IV) difficult. Even under the optimum conditions (cf. EXPERIMENTAL) the latter is obtained in yields not exceeding 25-27%.

The oxidation of compound (III) proceeds much better with potassium permanganate. In studying this reaction we varied widely the amount of oxidizing agent (from 100 to 300%), the amount of solvent and the nature of the medium, and also the temperature (from 0 to 45°). As a result it was established that the oxidation process should be run in acetic acid solution at 15-20°, taking a 1.5-fold amount of potassium permanganete, dissolved in 10% sulfuric acid. In this case the isolation of the ketone (IV) is realized very simply – after removal of the formed manganese dioxide by filtration the solution under cooling is neutralized with concentrated ammonia solution to pH 6-6.5, as a result of which all of the ketone (IV) precipitates from solution, here in such pure form that it can be used for subsequent transformations without additional purification. Here the yield of ketone (IV) is 50-53%, since independent of the oxidation conditions, the same as when chromic anhydride is used, a part of the original compound (III) always remains unchanged, while another part is oxidized to p-nitrobenzoic acid. The pure α-(dichloroacetamido)-β-hydroxy-p-nitropropiophenone (IV) has m. p. 124-125° (from benzene); $[\alpha]_D^{18} = -10.5°$ (c = 4 in C_2H_5OH). **

The third (last) step – the racemization and reduction of ketone (IV) – required especially detailed study. Here the simultaneous realization of both reactions proved to be the most desirable, i.e. the transformation of the ketone (IV) directly into the chloromycetin racemate (V). This we were able to achieve by running the process under the usual conditions for the Meerwein-Ponndorf reaction, using 1.5-2 moles of aluminum isopropylate in isopropyl alcohol medium. However, very pronounced tar formation was observed here, and in addition the reduction of the ketone (IV) proceeded at a faster rate than did its isomerization, as a result of which, together with the chloromycetin racemate (V), the original chloromycetin L-threo isomer (III) was formed in considerable amounts. Although increasing the amount of aluminum isopropylate to 5 moles led to some acceleration of the racemization process, still this acceleration was only slight. The addition of acetone, benzene and other substances to the reaction medium, which could have retarded the reduction process, failed to improve the situation. Sodium isopropylate proved to be a considerably more effective means, the addition of which in small, but strictly controlled amounts (0.14 mole), not only accelerated the racemization, but also sharply reduced the amount of tar formation. In the presence of the indicated amount of sodium isopropylate the amount of tar formation is extremely slight if the reaction is run at 60° for 6 hours, and is practically absent if the process is run at 37° for 24 hours. However, even under the last indicated most favorable conditions, the ketone (IV) succeeds in being partially reduced before it has a chance to be racemized, and consequently, together with the chloromycetin racemate (V), formed in about 45% yield, the chloromycetin L-threo isomer (III) is always obtained in 13-17% yield.* It should be mentioned that the separation of compound (V) from compound (III) is easily achieved with the aid of either ethyl acetate or dichloroethane, in which solvents compound (V) is considerably less soluble than is compound (III). The isolated racemate (V) can be used for subsequent conversion into the optically active chloromycetin (I) without additional purification by recrystallization.

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* In order to have a means of evaluating the amounts of formed ketone (IV) and p-nitrobenzoic acid, and also of the unreacted L-threo-N-dichloroacetamidodiol (III), we developed a procedure for the separation and determination of the three mentioned compounds. The procedure consists in the extraction from the reaction mass (previously diluted with water) of the ketone (IV) and p-nitrobenzoic acid with dichloroethane, a solvent in which compound (III) is insoluble. The latter is then extracted with ether, while the ketone (IV) and p-nitrobenzoic acid are separated by means of soda solution.

** The properties of this compound and its antipode were briefly described by us earlier [18].

Although methods for the direct conversion of the racemate (V) into the chloromycetin (I) are described in the literature [3, 12], still it is more advantageous to first hydrolyze the racemate to D,L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol, separate the latter into its antipodes, and then convert the isolated D-threo isomer into the chloromycetin (I). According to our data, the hydrolysis of the racemate (V) proceeds in 90% yield under the conditions of boiling it for 1 hour with 20% hydrochloric acid. Of the methods known at the present time for the separation of D,L-threo-1-(p-nitrophenyl-2-amino-1,3-propanediol into its antipodes and the conversion of the D-isomer into chloromycetin (I) [2-4, 6-10, 16], our method [2, 16], described in detail in the EXPERIMENTAL, remains one of the most successful, which with the acid of d-tartaric acid permits the rapid separation of the racemic aminodiol into its antipodes and then further permits the isolation of each of the antipodes in yields reaching 80-82%;** the subsequent N-dichloroacetylation of the D-antipode makes it possible to easily obtain chloromycetin (I) in 90-93% yield, since the L-antipode can again be subjected to racemization.

As a result, the studies made by us permitted solving for the first time the problem of converting the biologically inactive L-threo isomer (III) of chloromycetin into its active D-threo form (I).

EXPERIMENTAL

1. Preparation of Methyl Dichloroacetate

To 409 g (2.5 moles) of trichloroacetic acid in 0.5 liter of methyl alcohol with vigorous stirring was gradually added 200 g of 90% zinc dust (2.75 moles). The zinc dust was added over 2-3 hours, taking care that the temperature of the reaction mass was kept at 10-20°. Then the temperature was raised to 30° and the reaction mass was stirred at this temperature for 0.5 hour. After this the mixture was cooled to 15-20°, and the small amount of precipitate was filtered and washed in two portions with 50 ml of methyl alcohol. To the filtrate, containing dichloroacetic acid and zinc chloride, was gradually added 130 ml of concentrated sulfuric acid, in which connection the reaction mixture heated up strongly and at the same time a copious precipitate of zinc sulfate began to separate. After all of the sulfuric acid had been added the reaction mixture was boiled for 15 minutes, then cooled to 15-20°, and the thick mass poured into a mixture of 3.5 liters of water and 1 kg of ice. The resulting oil was separated and washed with water, then with 130 ml of 2% sodium bicarbonate solution and again with water, after which 10 g of anhydrous calcium chloride was added, which was removed by filtration after 2 hours. The yield of the methyl dichloroacetate was about 270 g, which was purified as follows. The ester was heated to 95° and to it was gradually added with stirring 27 g of dry pyridine, after which the reaction mixture was heated at 95-100° for 1 hour. The mass darkened rapidly and toward the end of heating had become brown. On conclusion of heating the reaction mass was cooled to 15-20°, acidified under stirring with 10% sulfuric acid until it showed acid to Congo, and then the mixture was steam-distilled. The lower distillate layer was separated and washed with 10% sulfuric acid, 2% sodium bicarbonate solution, and finally with water. The obtained methyl dichloroacetate was dried for a day over 27 g of anhydrous calcium chloride and then vacuum-distilled, collecting the fraction with b. p. 73-76° at 68-70 mm. Weight 186 g; yield 52%.

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* An attempt was made to divide the process into two stages – to first realize racemization, and then reduction of the ketone (IV). The racemization was run for 3-6 hours at 55-65° in different solvents (anhydrous isopropyl alcohol, acetone, benzene) and in the presence of sodium ethylate (from 0.14 to 1.4 moles) or aluminum isopropylate (from 0.25 to 5.2 moles), but in all of these cases less satisfactory results were obtained than those given above.

** The separation of the racemate is easily achieved due to the difference in the solubilities of the acid d-tartrates of D- and L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol in methyl alcohol and in water (the d,L-salt is more soluble than the d,D-salt), and due to the ability of the d,L-salt to form quite stable supersaturated solutions.

2. Preparation of L-threo-1-(p-Nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (III)

a) A mixture of 25 g of L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol (II), 15 ml of methyl dichloroacetate and 13 ml of dry isoamyl alcohol was heated with stirring to 84-86°. At this temperature the methyl alcohol, formed as the result of reaction, began to distill. In measure with removal of methyl alcohol by distillation the temperature of the mass gradually rose to 100-102°. After 20 minutes from the beginning of methyl alcohol distillation the reaction mixture was cooled to 95° and seeded. Crystallization began rapidly, the heat of which caused the temperature of the mass to again rise to 100-102°; at the same time some more methyl alcohol distilled (a total of 4.5-5 ml). Continuing the cooling, the temperature of the reaction mass was reduced to 40-50°. The still warm mass was rubbed, cooled to 15-20°, and allowed to stand at this temperature for 1 hour, after which the precipitate was transferred to a filter, pressed well, washed 3 times with dry dichloroethane (taking it in 17 ml portions) and, finally, 2-3 times with ice water. The obtained L-threo-1-(p-nitrophenyl-2-(dichloroacetamide)-1,3-propanediol (III) was dried at 50-70°. Weight 34.7 g (91%). M. p. 149-151°; $[\alpha]^{25}_{D} = -18.5°$ (c = 4.9 in C_2H_5OH).

b) A mixture of 20 g of the pure L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol (II), 13 ml of methyl dichloroacetate and 13 ml of anhydrous isopropyl alcohol was boiled under stirring for 1 hour; here the precipitate dissolved at first, but after some time a crystalline substance separated. The reaction mass was cooled to 75° and, adding to it 43 ml of water heated to 70-75°, again heated to the boil to dissolve the obtained precipitate. Then the solution was cooled to 60°, seeded, and the cooling contalnued down to 5°. At this temperature the reaction mass was stirred for an hour, after which the obtained precipitate was filtered, pressed well, first washed twice with 25% isopropyl alcohol, then 3-4 times with dichloroethane (each time taking 10 ml portions of the indicated solvents, cooled to 5°), and finally with ice water. The obtained L-threo-1-(p-nitrophenyl-2-(dichloroacetamido)-1,3-propanediol (III) was dried at 50-70°. Weight 27.9 g (91.5%). M; p. 149-151°; $[\alpha]^{25}_{D} = -18.6°$ (c = 4.9 in C_2H_5OH).

3. Preparation of α-(Dichloroacetamido)-β-hydroxy-p-nitropropiophanone (IV)

a) To a solution of 30 g of L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (III) in 300 ml of glacial acetic acid under constant stirring was added over 45 minutes a solution of 14.6 g of potassium permanganate in 225 ml of 10% sulfuric acid, taking care that the temperature of the reaction mass was kept at 15-20°. After all of the oxidizing agent had been added the stirring was continued for another 15 minutes, then 300 ml of water was added, and the mixture kept at 15-20° for 30 minutes without stirring. The obtained manganese dioxide precipitate was filtered and washed 3 times with water, each time taken in 15 ml portions. The completely clear, almost colorless, filtrate was combined with the wash waters and then cooled to 5°, where the ketone (IV) usually began to precipitate. To the cooled reaction mixture at 5-10° and vigorous stirring was added over 2-3 hours a concentrated aqueous ammonia solution. The amount of precipitated ketone (IV) quickly increased. The addition of ammonia was continued to a pH of 6-6.5 (by Universal indicator), for which about 400 ml of ammonia solution was required. The reaction mass was cooled to −3° and held at this temperature for 30 minutes. The resulting ketone (IV) (precipitate) was filtered, pressed, and washed with ice water until sulfate ions were absent in the filtering. The well pressed precipitate was vacuum-dired at 25-35°. There was obtained 15.6 g of α-(dichloroacetamido)-β-hydroxy-p-nitropropiophenone (IV). Yield 52%. M. p. 117-121°.

b) To a mixture of 30 g of L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (III), 90 ml of dichloroethane and 30 ml of glacial acetic acid was added over 6 hours with constant stirring, a solution of 15 g of chromic anhydride in 30 ml of water, the temperature of the reaction mixture being maintained at 40-45°. As the oxidizing agent was added, the precipitate of the L-threo compound (III) gradually dissolved. After all of the chromic anhydride had been added the reaction solution was held at 40-45° for 1 hour, after which it was poured into 450 ml of water, and then extracted 5 times with dichloroethane, taking the latter in 150 ml portions. The thus obtained dichloroethane solution was washed 2-3 times with 10% aqueous soda solution and then with water, after which the dichloroethane was removed by distillation (at the end *in vacuo*). The oily residue was boiled for 30 minutes with 60 ml of chloroform and, having cooled the mixture to 5°, held at this temperature for 1 hour, after which the precipitate was filtered and washed with 10 ml of chloroform. This operation was repeated twice, each time heating the precipitate with 20 ml of chloroform and taking the latter in 5 ml portions for washing. There was obtained 8.1 g of α-(dichloroacetamido)-β-hydroxy-p-nitropropiophenone (IV) with m. p. 117-121°. Yield 27%.

4. Preparation of D,L-Threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (V)

To a hot solution of 50 g of aluminum isopropylate in 130 ml of anhydrous isopropyl alcohol was added a solution of sodium isopropylate, prepared by dissolving 0.15 g of metallic sodium in 26 ml of boiling anhydrous isopropyl alcohol, containing 0.8 g of aluminum isopropylate. The mixture, having been boiled for 5-10 minutes, was cooled to 60° and with vigorous stirring to it was gradually added 15.6 g of α-(dichloroacetamido)-β-hydroxy-p-nitropropiophenone (IV) with m. p. 117-121°, after which stirring of the reaction mass was continued at 60° for 6 hours. On conclusion of this to the orange solution with strong stirring and temperature not exceeding 60° was added a solution of 0.8 g of concentrated sulfuric acid in 45 ml of water; here a yellow precipitate was obtained. The reaction mass was boiled for 1 hour, after which it was filtered hot. The precipitate was broken up, boiled under stirring for 30 minutes with 150 ml of 80% isopropyl alcohol, and filtered hot. This operation was repeated twice more with new portions of 80% isopropyl alcohol, taking it each time in 150 ml portions. The reaction solution and the filtrate from the first extraction were combined and boiled for 30 minutes with 2 g of activated charcoal. The charcoal was filtered and washed with 20 ml of hot 80% isopropyl alcohol. The obtained filtrate, wash alcohol, and filtrates from the second and third extractions were combined and evaporated to dryness *in vacuo* at a bath temperature of 60-70°. The residue was crushed, treated with 15 ml of ethyl acetate and boiled for 30 minutes, after which it was cooled to 0° and kept at this temperature for 2 hours. The precipitate was filtered and washed, first in three doeses with 9 ml of ethyl acetate cooled to 0-2°, then in three doses with 12 ml of dichloroethane cooled to 0-2 °, and finally with ice water. This gave 7.1 g (45%) of D,L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (V) with m. p. 149-151°; after recrystallization from isoamyl alcohol the m. p. was 152-152°.

All of the ethyl acetate and dichloroacetane solutions were combined and evaporated *in vacuo* to dryness. To the obtained oily residue was added 12-15 ml of dichloroethane, the mixture allowed to stand for 1 hour at 12-15°, and the separated precipitate filtered. Recrystallization from water with the use of activated charcoal gave 2.0 g (13%) of L-threo-1-(p-nitrophenyl-2-(dichloroacetamido)-1,3-propanediol (III) with m. p. 151-152°.

5. Preparation of D,L-Threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol

A mixture of 10 g of the D,L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (V) obtained in Experiment 4, with m. p. 149-151°, and 20 ml of 20% hydrochloric acid was boiled for 1 hour, after which the obtained solution was cooled to 5° and kept at this temperature for 2 hours. The resulting hydrochloride (precipitate) was filtered and washed on the filter 3 times with dichloroethane, the latter being taken in 3 ml portions each time (cf. [19]). The precipitate was dissolved with heating in 20 ml of water, 0.3 g of activated charcoal added, the mixture boiled 10 minutes, filtered, and to the filtrate, cooled to 15-20°, was added with stirring 10% aqueous sodium hydroxide solution to pH 10-10.5; about 22 ml of alkali solution was required. After 2 hours at 10-15° the precipitate was filtered and washed 2-3 times with ice water, taking it each time in 3-5 ml portions, weight 5.9 g (90%). The obtained D,L-threo-1-(p-nitrophenyl)2-amino-1,3-propanediol had m. p. 140-142°.

6. Separation of D,L-Threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol Into Its Antipodes

a) Thirty grams of D,L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol was dissolved in 270 ml of boiling methyl alcohol and to this solution was added at one time under stirring 26.5 g (25% excess) of well pulverized d-tartaric acid. A mixture of the acid d-tartrates of the D- and L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediols quickly precipitated from the solution. The reaction mass was boiled for 1 hour, then cooled to 20°, and stirred at this temperature for another hour. The precipitate was filtered and washed twice with methyl alcohol, taking the latter in 15 ml portions for each washing.

The obtained cake of mixed salts was boiled under stirring with 500 ml of methyl alcohol for 1.5 hours, cooled to 20°, and the stirring continued at this temperature for 30 minutes. The precipitate was filtered and washed 3 times with methyl alcohol, taking the latter in 15 ml portions for each washing. The decomposition temperature of the salt was 182-184°. The well pressed cake was extracted a second time under the same conditions with 150 ml of methyl alcohol. After cooling, filtration, and washing with methyl alcohol (3 times with 10 ml portions) the pure acid d-tartrate of D-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol was obtained with

m. p. 186-187° (decompn). Weight 23.6 g (92%). *

The obtained salt was dissolved at 60-70° in 240 ml of water, 0.4 g of activated charcoal added to the solution, the hot solution stirred for 10 minutes, and the charcoal filtered and washed on the filter with 20 ml of hot water. The filtrate, combined with the wash waters, was cooled (usually the salt begins to crystallize here) and with stirring a concentrated aqueous ammonia solution was added slowly, taking care that the temperature of the mixture did not rise above 20°. Here the salt dissolved completely at first, and then the amine began to separate. The ammonia addition was terminated when distinct alkaline reaction to phenolphthalein was reached, for which about 13 ml of 25% aqueous ammonia solution was required. Then the reaction mixture was cooled to 10° and stirred at this temperature for 2 hours, periodically checking for alkalinity of the medium. The resulting precipitate was filtered and washed twice with ice water, taken each time in 10 ml portions. The obtained D-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol was first dried at 50-60°, and at the end at 70-80°. Weight 12 g, which represents an 87% yield, based on bitratrate taken for the decomposition, or 80%, based on the D-threo-aminodiol contained in the original racemic amine. M. p. 161-162°. **

b) In 75 ml of water at 85° was successively dissolved under stirring 30 g of D,L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol and 26.5 g of d-tartartic acid. The reaction solution was heated at 70° for 1 hour, after which it was cooled to 60° and 150 ml of methyl alcohol was added. The acid d-tartrates of the D- and L-threo-aminodiols separated on cooling to 0°. For more complete crystallization of these salts the reaction mixture was kept at 0° for 1 hour. The thick slurry was again heated to 45-50° and then stirred at this temperature for 30 minutes, where the bitratrates of the L-threo-aminodiol was preferentially dissolved. The undissolved precipitate was filtered on a previously heated Buchner funnel, washing the reaction flask with the mother liquor, warmed to 45-50°. The precipitate was washed in three doses with 65 ml of methyl alcohol and dried. Weight 27 g; m. p. 178-182° (decompn). The obtained salt was crushed well and boiled with 150 ml of methyl alcohol for 1 hour, after which the mass was cooled to 10° and stirred at this temperature for another hour. The precipitate of the acid d-tartrate of D-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol was filtered and washed in two doses with 45 ml of methyl alcohol; Weight 23.2 g (90.5%); m. p. 186-187° (decompn). *** The D-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol is isolated from the obtained salt by the method described in Experiment 6a.

c) To isolate the L-threo-1-(p-nitrophenyl-2-amino-1,3-propanediol (II), all of the mother liquors obtained in Experiment 6a and 6b and containing the acid d-tartrate of this amine, a small amount of the acid d-tartrate of the corresponding racemate, and also some d-tartaric acid, were evaporated in vacuo. The residue, a viscous light-brown mass, was dissolved at 70° in 180 ml of water and, having added 1 g of activated charcoal to the hot solution, was stirred for 10-15 minutes, after which it was filtered. The charcoal was washed on the filter with 25 ml of hot water. The filtrate together with the wash waters was cooled to 20° and the L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol (II) precipitated with ammonia under the conditions described for the isolation of the D-threo isomer (cf. Experiment 6a). The yield of the L-threo-aminodiol (II) was 12-13 g, with the corresponding racemate and ammonium tartrate being present as impurities. The L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol with m. p. 163-164° can be obtained pure by recrystallization from water. However, for realizing the above described racemization of the L-threo-aminodiol (II) in Experiments 2, 3, and 4 this purification is superfluous, since the ammonium acid tartrate is easily separated at the stage of N-dichloroacetylation of the amine (Experiment 2); while the racemic amine in general cannot disturb the process; to be sure, it is necessary to keep in mind that the presence of the racemate does not permit controlling the purity of the obtained intermediate products by their constants.

7. Preparation of D-Threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol (Chloromycetin, Levomycetin (I)

The dichloroacetylation of the D-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol should be run under the same conditions as described in Experiment 2. If the starting D-threo-aminodiol does not melt below 161°, then the isolated chloromycetin has m. p. 149-151° and $[\alpha]^{25}_{D}$ = +18.5° (±0.5°) (c = 4.9 in C_2H_5OH). It satisfies its assignment pharmacopoeia requirements and its additional purification by recrystallization is superfluous. The yield of the chloromycetin reaches 90-93%.

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* If the decomposition temperature of the salt proves to be below 186° after the second extraction, then the cake should be subjected to a third extraction with 65 ml of methyl alcohol under the same conditions. Three washings with methyl alcohol are made, each time with 8 ml portions.

** If the melting point of the obtained amine is lower than the indicated, but not below 158°, then the amine should be stirred for 2 hours at 20° with a 12-fold amount of water. If the melting point of the amine is even lower, then it becomes necessary to recrystallize the amine from water.

*** If the isolated salt has a decomposition temperature lower than 186-187°, then, as in Experiment 6a, it should be given another extraction with 65 ml of methyl alcohol.

SUMMARY

The racemization of L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol and subsequent conversion of the obtained racemate into chloromycetin (levomycetin) were realized.

The racemization of the L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol proved possible only after one of the centers of asymmetry in the molecule was destroyed, with the simultaneous introduction of a grouping that facilitated the racemization of the second center; the latter process was run simultaneously with the reduction of the first center of asymmetry. In accord with what has been said the L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol, obtained as a nonusable by-product in the synthesis of chloromycetin, was converted by heating with methyl dichloroacetate into L-threo-1-(p-nitrophenyl-2-(dichloroacetamido)-1,3-propanediol, and the latter was oxidized with potassium permanganate (or chromic acid) to the optically active α-(dichloroacetamido)-β-hydroxy-p-nitropropiophenone, which was then subjected to simultaneous racemization and reduction with the aid of aluminum and sodium isopropylates in isopropyl alcohol medium. The subsequent conversion of the obtained D,L-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol into chloromycetin was realized by the method of its hydrolysis to D,L-threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol, which was then separated into its antipodes through the acid d-tartrates, while the isolated D-threo osomer was subjected to N-dichloroacetylation by heating it with methyl dichloroacetate.

As a result, for the first time the problem of converting its biologically inactive L-threo isomer into chloromycetin was volved.

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THE MIGRATION OF THE PEPTIDE RESIDUE IN PEPTIDE OF SERINE

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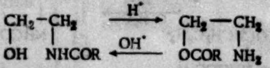
One of the specific characteristics of the acyl derivatives of amino alcohols and hydroxy amino acids, having the hydroxy and amino groups in vicinal position, is the ability of the acyl residue to migrate from the nitrogen to the oxygen, and from the oxygen to the nitrogen.



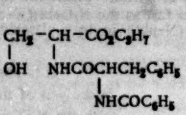
$$\underset{OH}{CH_2}-\underset{NHCOR}{CH_2} \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \underset{OCOR}{CH_2}-\underset{NH_2}{CH_2}$$

This reaction, studied in detail by a large number of investigators [1], attracted special attention recently, since the O-acyl derivatives of the alkanolamines have found wide use in medicine [2].

Recently, on the example of ethanolamine we showed that similar migration can proceed not only with the acyl, but also with the peptide (aminoacyl) residue [3].

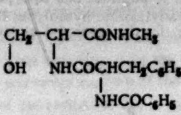
In the present work experiments were performed on the migration of the aminoacyl residue in the peptides of serine and its derivatives. A study of such reactions for serine peptides is of interest in connection with the investigation of the specific properties of the β-hydroxy amino acids. In recent years a number of studies have appeared, in which the migration of the peptide residue in the peptides of hydroxy amino acids during the time of acid hydrolysis of proteins was demonstrated [4].

The study subjects in the present work were the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine (I), the methylamide of N-(N-benzoyl-3-phenylalanyl)serine (II), and the methylamide of N-[N-(p-toluenesulfonyl)glycyl] serine (III): [6].



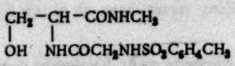
$$\underset{OH}{CH_2}-\underset{NHCO\underset{NHCOC_6H_5}{CH}CH_2C_6H_5}{CH}-CO_2C_3H_7$$

(I)



$$\underset{OH}{CH_2}-\underset{NHCO\underset{NHCOC_6H_5}{CH}CH_2C_6H_5}{CH}-CONHCH_3$$

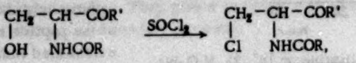
(II)



$$\underset{OH}{CH_2}-\underset{NHCOCH_2NHSO_2C_6H_4CH_3}{CH}-CONHCH_3$$

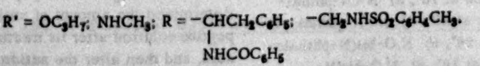
(III)

The experiments on the migration of the aminoacyl residue were run with the aid of thionyl chloride, with hydrogen chloride in either alcohol or dioxane solution, and with phosphorus pentachloride. Here the serine peptides were converted into derivatives of β-chloroalanine:



$$\underset{OH}{CH_2}-\underset{NHCOR}{CH}-COR' \xrightarrow{SOCl_2} \underset{Cl}{CH_2}-\underset{NHCOR,}{CH}-COR'$$

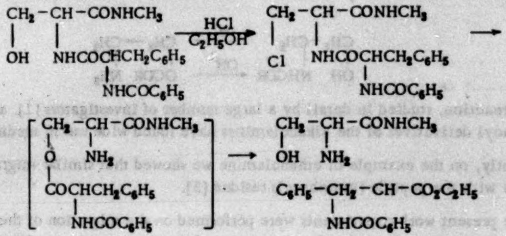
where



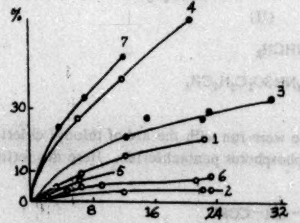
$$R' = OC_3H_7;\ NHCH_3;\ R = -\underset{NHCOC_6H_5}{CH}CH_2C_6H_5;\ \ -CH_2NHSO_2C_6H_4CH_3.$$

In not a single instance could the presence of oxazoline derivatives be revealed. As a result, the esters and amides of the acylated serine peptides behaved the same as the ethanolamine derivative: as the result of reaction there arose the β-chloro derivatives of amino acids. However, in contrast to the aminoacyl derivatives of β-chloroethylamine, which are readily converted under the influence of water into the O-peptides of ethanolamine, the β-chloro derivatives of the peptides of alanine are saponified under these conditions to the starting serine peptides. Thus, the heating of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine for 2 hours with aqueous dioxane gave the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine, while the heating of the methylamide of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine with 50% alcohol gave the methylamide of N-(N-benzoyl-3-phenylalanyl)serine. In both cases the presence of amino nitrogen in the reaction solution could not be revealed; these facts are evidence that the peptide residue failed to migrate.

When the methylamide of N-(N-benzoyl-3-phenylalanyl)serine was treated with hydrogen chloride in anhydrous alcohol the main reaction products were the methylamide of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine and the ethyl ester of N-benzoyl-3-phenylalanine. Apparently, in this case the unstable methylamide of O-(N-benzoyl-3-phenylalanyl)serine is formed, which under the influence of the alcohol decomposes with the formation of the ethyl ester of N-benzoyl-3-phenylalanine:



The migration of the aminoacyl residue was qualitatively shown under the influence of conc. HCl on N-(N-acetyl-3-phenylalanyl)serine. Here the appearance of the hydroxamic reaction is distinct, which testifies to the formation of the ester bond. The resulting O-peptide is very unstable. The peptide is preponderantly hydrolyzed to serine and the acylated amino acid. Thus, 26-28% of the amino groups are liberated when the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine is treated with conc. HCl, of which 72% belongs to serine. A somewhat indirect indication that the aminoacyl residue migrates under the influence of HCl is the difference in the hydrolysis rate of the N-peptides and N,O-peptides of serine. Under the influence of conc. HCl the N-(N-acetyl-3-phenylalanyl)serine hydrolyzes twice as fast as the N,O-bis(N-acetyl-3-phenylalanyl)serine. This difference is even sharper for the isopropyl esters of N-(N-phthaloylglycyl)serine and N,O-bis(N-phthaloylglycyl) serine (see Figure).



1) N-(N-acetyl-3-phenylalanyl)serine at 18°, 2) N,O-bis (N-acetyl-3-phenylalanyl)serine at 18°, 3) N-(N-phthaloylglycyl)serine isopropyl ester at 18°, 4) N-(N-phthaloylglycyl)serine isopropyl ester at 26°, 5) N,O-bis(N-phthaloylglycyl)serine isopropyl ester at 18°, 6) N,O-bis(N-phthaloylglycyl)serine isopropyl ester at 26°, 7) N-(N-benzoyl-3-phenylalanyl)serine isopropyl ester at 26°.

It is possible that the greater ease of hydrolysis of the serine N-peptides when compared with the N,O-peptides is due to prior migration of the peptide residue. Such migration, characteristic for the N-acyl derivatives of serine, cannot occur for the N,O-diacyl derivatives of hydroxyl amino acids. If the postulation is valid that the hydrolysis proceeds through the O-peptide stage, then the exclusion of water from the reaction mixture may facilitate the catching of the O-peptide. For this purpose a number of experiments were made with sulfuric acid; here we were able to realize migration of the peptide residue; the rearrangement was established indirectly by the change in the amount of amino nitrogen in the peptide solution. Having determined the amount of amino nitrogen in the peptide solution after its treatment with sulfuric acid, and then after the action of alkali on the acid solution, it becomes possible to establish the degree of migration of the peptide residue from the nitrogen to oxygen and from oxygen to nitrogen. The isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine, the methylamide of N-(N-benzoyl-3-phenylalanyl)serine and the methylamide of N-[N-(p-toluenesulfonyl)glycyl] serine were treated with sulfuric acid, and the amounts of

TABLE 1

Name of Substance	Reagent	Time	Temperature	Amino Nitrogen* (in %)		Migration (in %)
				after treatment with acid	after treatment with alkali	
N-(N-Benzoyl-3-phenylalanyl)serine isopropyl ester	Oleum	2 min.	50°	50	25	50
	Oleum	2 days	18	42	25	40
	100% H_2SO_4	10 min.	50	23	17	26
	100% H_2SO_4	3 hours	50	78	43	45
	100% H_2SO_4	3 days	18	41	26	37
N-(N-Benzoyl-3-phenylalanyl)serine methylamide	0.14 N Sulfuric acid in dioxane	1 hour	50	106	68	38
		1 hour	100	70	33	53
		2 hours	100	65	30	54
N-[N-(p-Toluenesulfonyl)glycyl]serine methylamide		1.5 hours	100	50	6	88
		2.5 hours	100	70	37	47

amino nitrogen and serine in the solution determined. An aliquot portion of the solution was treated with alkali, and the amount of amino nitrogen in the solution again determined. The determination results are given in Table 1. From the obtained results it follows that under the influence of sulfuric acid on serine derivatives the appearance of amino nitrogen is observed in all cases. The peptide solutions that were treated with sulfuric acid failed to contain serine, but gave a positive reaction for pyrotartaric acid and the double bond. These facts indicate that the migration reaction under the influence of sulfuric acid is not accompanied by hydrolysis of the peptides, but that together with the formation of the O-peptide there occurs dehydration and the appearance of aminoacrylic acid derivatives. It was established by means of special experiments that under the conditions for the Van Slyke determination of amino nitrogen the acyl derivatives of aminoacrylic acid are decomposed with the evolution of nitrogen; consequently, the measure of the number of amino groups, appearing as the result of the peptide residue migrating from nitrogen to oxygen, is only the difference between the determination of amino nitrogen in the solution before and after its treatment with alkali. The percent migration of the peptide residue from nitrogen to oxygen is calculated in the last column of Table 1. In not a single case did the migration reach 100% and it depended on the character of treating the peptide with sulfuric acid. The process went to greatest completion in the experiments with 0.14 N sulfuric acid in dioxane. Under the influence of the acid there was revealed 50% of the amino groups, which vanished nearly 100% after treatment with alkali. The degree of conversion of the N-peptide into the O-peptide was 88%. Apparently, the migration is accompanied by side reactions, which, probably, are not limited to the one phenomenon of dehydration. It should be mentioned that in the experiments performed by Desnuelle on proteins, the migration also failed to be complete.

When the present investigation had already been completed, there appeared in print the work of Elliott, in which the author effected the migration of the peptide residues in silk fibroin with the aid of H_2SO_4, and established that the migration of the peptide residue proceeds to the extent of 61%. In this manner the results, obtained by us on the peptides of serine, by Elliott on silk fibroin, and earlier by Desnuelle [4] on a number of other proteins, all established the ability for migration of the peptide residue under the influence of sulfuric and hydrochloric acids. However, these results should be regarded as being preliminary. They give a qualitative picture of the migration process, which undoubtedly is accompanied by a number of secondary processes.

EXPERIMENTAL

Conversion of the N-Peptide Derivatives of Serine Into the N-Peptide Derivatives of β-Chloroalanine

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* The amino nitrogen, corresponding to the complete conversion of the N-peptide into the O-peptide, was taken as 100%.

TABLE 2

Weight (in g)*	Reaction conditions		Amino nitrogen (in %)**
	Time (in hrs.)	Temperature	
N-(N-Acetyl-3-phenylalanyl) serine			
0.0334	3	18°	4.5
0.0305	6	18	8.0
0.0296	12	18	14
0.0317	24	18	18.7
N,O-Bis(N-acetyl-3-phenylalanyl)serine			
0.0311	3	18	2.5
0.0533	6	18	3.9
0.0556	9	18	5.0
N-(N-Phthaloylglycyl)serine Isopropyl Ester			
0.0227	2	18	–
0.0282	12	18	20.5
0.0305	22	18	25
0.0311	31	18	32
0.0299	6	26	26
0.0325	12	26	38
0.0251	23	26	58
N,O-Bis(N-phthaloylglycyl)serine Isopropyl Ester			
0.0162	23	18	3.6
0.01665	6	26	6
0.0310	21	26	6.3
0.0250	23	26	7.4
N-(N-Benzoyl-3-phenylalanyl)serine Isopropyl Ester			
0.0256	4	26	28
0.0469	7	26	33
0.0439	12	26	46

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* The weight corresponds to the aliquot portion taken for determination of the amino nitrogen.

** The amino nitrogen, formed in the hydrolysis of the peptide group, is taken as 100%.

N-(N-Benzoyl-3-phenylalanyl)-β-chloroalanine Isopropyl Ester.

a) A mixture of 0.5 g of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl) serine (m. p. 168°) and 5 ml of thionyl chloride was heated at the boil for 3 minutes. Dilution of the reaction mixture with anhydrous ether gave crystals of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine. M. p. 157°. The substance is unknown in the literature.

Found %: C 62.42, 62.33; H 6.11, 6.03; N 6.59, 6.66; Cl 9.16, 9.07. $C_{22}H_{25}O_4N_2Cl$. Calculated %: C 62.46; H 6.01; N 6.73; Cl 8.52.

b) Hydrogen chloride gas was passed for 2 hours into a solution of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)-serine in anhydrous dioxane. Dilution with water gave a precipitate of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine. M. p. 155°. Its mixed melting point with the compound obtained in the preceding experiment failed to be depressed.

The isopropyl ester of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine was heated for 2 hours in aqueous-dioxane solution. Dilution of the reaction mass with water gave crystals of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine. M. p. 168°.. Its mixed melting point with the earlier obtained isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine failed to be depressed. The amount of amino nitrogen was determined by the Van Slyke method in an aliquot portion of the solution, while the amount of hydrochloric acid was determined by titration.

Found %: amino nitrogen 6, 4, 5. Calculated %: 100 (calculated on the basis of complete convertion of the N-peptide into the O-peptide).

0.0838 g substance: consumed 2.05 ml of 0.1 N NaOH; 0.1525 g substance: consumed 3.40 ml 0.1 N NaOH. Calculated: 2.01, 3.65 ml.

N-(N-Benzoyl-3-phenylalanyl)-β-chloroalanine Methylamide.

a) The N-(N-benzoyl-3-phenylalanyl)serine methylamide (0.8 g) was dissolved in 3 ml of thionyl chloride cooled to 0° and then allowed to stand for 1 hour in the cold. After treatment with 25 ml of ether there was obtained 0.9 g of white amorphous substance with m. p. 135-137°. On standing it evolved sulfur dioxide gas. The substance gave a copious precipitate of silver chloride with silver nitrate. Under the influence of water it was converted into the starting methylamide of N-(N-benzoyl-3-phenylalanyl)serine. Apparently, this compound was the β-chlorosulfinyl derivative of the methylamide of N-(N-benzoyl-3-phenylalanyl)alanine. The compound was not studied further.

b) The chlorosulfinyl derivative (0.8 g) of the methylamide of N-(N-benzoyl-3-phenylalanhl)alanine was dissolved in 5 ml of acetic acid heated to 100°, after which the solution was treated with 5 ml of water. Cooling gave needle crystals of the methylamide of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine. M. p. 199°. The substance is not described in the literature.

Found %: Cl 9.10, 9.08; N 10.82, 10.92. $C_{20}H_{22}O_3N_3Cl$. Calculated %: Cl 9.16; N 10.84.

c) The methylamide (0.8 g) of N-(N-benzoyl-3-phenylalanyl)-serine was mixed with 3 ml of thionyl chloride and heated at 60° until dissolved. To the reaction mixture after 14 hours was added 20 ml of ether. Here 0.85 g of the methylamide of N-(N-benzoyl-3-phenylalanyl)-β-chloroalinine separated. After recrystallization from a mixture of alcohol and butyl acetate the m.p. was 199-200°. Its mixted melting point with the compound described in Experment "b" failed to be depressed.

d) A mixture of 0.8 g of the methylamide of N-(N-benzoyl-3-phenylalanyl)serine and 0.17 g of phosphorus pentachloride in 10 ml of chloroform was stirred at room temperature to almost complete solution. Treatment with ether gave needle crystals, which were recrystallized from aqueous acetic acid. The yield of the methylamide of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine was 0.2 g. Its mixed melting point with the preparation described in Experiment "b" failed to be depressed.

e) A solution of 0.9 g of the methylamide of N-(N-benzoyl-3-phenylalanyl)serine in 5 ml of anhydrous alcohol was saturated under cooling with hydrogen chloride, and then heated for 1.5 hours at 70°. After removal of the alcohol the oily residue was made to crystallize by rubbing with ether, and the thus obtained crystals recrystallized from aqueous acetic acid. The yield of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine was 0.6 g. M. p. 198°. Its mixed melting point with the preparation obtained in Experiment "b" fails to be depressed. Evaporation of the mother liquor and recrystallization of the obtained crystals from 50% alcohol gave 0.1 g of the benzoylphenylalanine ester.

f) A solution of 0.2 g of the methylamide of N-(N-benzoyl-3-phenylalanyl)serine in 5 ml of dioxane was saturated with hydrogen chloride and allowed to stand for 2 hours at room temperature. After evaporation of the dioxane *in vacuo* the oily residue was treated as in Experiment "e". The yield of the methylamide of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine was 0.1 g, m. p. 195°. Its mixed melting point with the preparation obtained in Experiment "b" failed to be depressed.

The methylamide (0.2 g) of N-(N-benzoyl-3-phenylalanyl)-β-chloroalanine was heated for 2 hours at 100° with 4 ml of 50% alcohol. Reduction to small volume gave crystals of the methylamide of N-(N-benzoyl-3-phenylalanyl)serine. Its mixed melting point with the synthetic product failed to be depressed. The filtrate, remaining after removal of the methylamide of N-(N-benzoyl-3-phenylalanyl)serine, failed to show the presence of amino nitrogen.

Migration of the Peptide Residue Under the Influence of Concentrated HCl

a) Comparison of the Hydrolysis Rates of the N-Peptides and N,O-Peptides of Serine. The weighed samples of the serine N-peptides and N,O-peptides were each treated with 0.5 ml of hydrochloric acid (d 1.19) and then allowed to stand in the thermostat at 18 and 26°. After definite time intervals the amounts of amino nitrogen in an aliquot portion of the solution were determined by the Van Slyke method. The analysis results are given in Table 2.

b) Determination of the Amount of Serine in the Hydrolyzate. The isopropyl ester (0.4004 g) of N-(N-benzoyl-3-phenylalanyl)serine was hydrolyzed with concentrated hydrochloric acid at 26° for 6 hours. The solution was made up of 25 ml, and the amount of serine in 2.5 ml was determined by the periodate method.

For binding the ammonia there was consumed: 2.01 and 1.98 ml of 0.025 N H_2SO_4. Found serine in %: 20.1, 19.8.

The amount of amino nitrogen in an aliquot portion of the solution was determined by the Van Slyke method.

The amount of evolved nitrogen: 1.77 and 1.72 mg. Found amino groups in % : 28.26.

Influence of Concentrated Sulfuric Acid on the N-Peptide Derivatives of Serine

The weighed samples of the isopropyl ester of N-(N-benzoyl-3-phenylalanyl)serine, the methylamide of N-(N-benzoyl-3-phenylalanyl)serine and the methylamide of N-[N-(p-toluenesulfonyl)-glycyl]serine [6] were treated with sulfuric acid under the conditions given in Table 2. After definite time intervals the amounts of amino nitrogen in the solutions were determined by the Van Slyke method. An aliquot portion of the solution was treated under strong cooling with 20% alkali solution to pH 1-2, and then with 0.2 N alkali solution to pH 8.5, after which the amount of amino nitrogen present was again determined. The determination results are given in Table 3.

TABLE 3

Weight* (in g)	Acid treatment conditions	Conditions of alkali treatment	Amino nitrogen** (in %)	
			of the sample weight	of total N
N-(N-Benzoyl-3-phenylalanyl)serine Isopropyl Ester				
0.0229	Heating with oleum for 2 minutes at 50°	–	1.73, 1.42	50, 42
		pH 8.5, 18°	0.83, 0.83	23, 25
0.0319	10 minutes at 50° with 100% H_2SO_4	–	0.80, 0.83	23, 23.5
		pH 8.5, 18	0.60, 0.60	17, 17
0.0198	72 hours at 18° with 100% H_2SO_4	–	1.51, 1.37	43, 39
		pH 8.5, 18	0.86, 0.94	24, 27
0.0125	48 hours at 18° with oleum	–	1.58, 1.42	45, 41
		pH 8.5, 18	0.92	26
0.0236	3 hours at 50° with 100% H_2SO_4	–	2.71, 2.77	77, 79
		pH 8.5, 18	1.51, 1.51	43, 43
0.0186	0.14 N sulfuric acid solution in anhydrous dioxane for 3 hours on the water bath and overnight at room temperature	–	3.62, 3.75	103, 109
		pH 8.5, 18	3.64	104
0.0079	2 hours at 50° with 0.147 N H_2SO_4 in anhydrous dioxane	–	3.8, 3.66	110, 106
		pH 8.5, 18	3.7	107
0.0175	12 hours at 18° with 0.1 N H_2SO_4 in anhydrous dioxane	–	1.88, 2.15	62, 61
		pH 8.5, 18	2.02	58
N-(N-Benzoyl-3-phenylalanyl)serine Methylamide				
0.0959	Conc. H_2SO_4 for 1 hour at 50°	–	6.9, 7.6	102, 110
		pH 9, 18°	5.2, 4.3	75, 61
0.2900	5.35 ml of 0.14 N H_2SO_4 in dioxane, 1 hour at 100°	–	5.4, 5.4	70, 71
		pH 9, 18	1.4, 1.4	33, 30
0.2900	5.35 ml of 0.14 N H_2SO_4 in dioxane, 2 hours at 100°	–	4.8, 5.0	64, 66
		pH 9, 18	2.3, 2.0	31, 30
N-[N-(p-Toluenesulfonyl)glycyl]serine Methylamide				
0.3556	8 ml of 0.14 N H_2SO_4 in dioxane at 100° for 1.5 hours	–	3.6, 3.9	50, 55
		pH 9, 18°	0.45, 0.5	6, 7
0.3556	8 ml of 0.14 N H_2SO_4 in dioxane at 100° for 2.5 hours	–	4.5, 0.5	70, 71
		pH 9, 18	1.3, 1.3	38, 36

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* The weight corresponds to the aliquot portion taken for determination of the amino nitrogen.

** The amino nitrogen, corresponding to the complete conversion of the N-peptide of serine into the O-peptide, is taken as 100 %.

SUMMARY

The reaction for the migration of the acylaminoacyl (peptide) residue in peptide derivatives of serine was studied. When the peptide derivatives of serine are reacted with thionyl chloride, or with hydrogen chloride in either alcohol or dioxane solution, the β-chloro derivatives of the peptides of alanine are formed, which in aqueous medium are converted into the original compounds. Under the influence of concentrated hydrochloric acid there apparently occurs migration of the peptide residue from nitrogen to oxygen, since the N-peptides of serine are hydrolyzed more rapidly than are the N,O-peptides. Two reactions are observed when the peptide derivatives of serine are treated with either sulfuric acid or oleum – the migration of the acylaminoacyl residue from nitrogen to oxygen, and the dehydration of the serine peptides.

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* T. p. = C. B. Translation pagination.

THE THERMAL STABILITY OF COBALT AND NICKEL HALIDES

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An examination of the halides of the Fe, Co and Ni triad shows that, in the case of iron, compounds have been prepared with fluorine, chlorine, and iodine corresponding to valencies of both two and three; in the transition to cobalt and then to nickel, the lower valency, two, becomes increasingly prominent. In the case of cobalt the compound CoF_3 is also known (prepared by the action of fluorine on the difluoride or on metallic cobalt, stable in the solid, liquid, and gas states) and also $CoCl_3$ which was apparently prepared in 1952 by Schäfer and Krehl [1] in the form of a gas by passing a current of chlorine over $CoCl_2$ at temperatures above 645°; it was shown that the amount of cobalt carried over by the gas stream was greater than would correspond to the vapor pressure of $CoCl_2$. Schäfer and Krehl tentatively attribute the formula $CoCl_3$ to the compound, and give the value of the equilibrium constant $K = \frac{P^2_{CoCl_3}}{P^2_{CoCl_2} \cdot P_{Cl_2}}$ in the temperature range 645-800° C.

The bromides and iodides of cobalt known at present correspond to the bivalent state of oxidation only.

In the case of nickel the NiX_3 compounds are still less stable, and even NiF_3 has not yet been obtained. Only compounds of the type NiX_2 are known for all the four nickel halides.

In a search for a solution to the problem of valency decrease in the transition from iron to nickel, we made a comparative study of certain thermodynamic data for cobalt and nickel chlorides and bromides*, namely the thermal dissociation pressures of these halides and the values of the free energy, enthalpy, and entropy of their formation.

As the dissociation pressure of the compounds studied is very low, its direct determination is difficult and it is more conveniently determined by an indirect method, for example by the study of some reaction which involves the given halide. We used the reduction of the compounds by hydrogen, so that the reaction equilibrium

$$MeX_2 + H_2 \rightleftharpoons Me + 2HX.$$

was studied.

This is a suitable choice, as the pressure of the halogen in the thermal dissociation of the halides studied is less than the pressure of the halogen which corresponds to the thermal dissociation of the corresponding hydrogen halide; otherwise hydrogen would completely reduce the halide, and the reaction would be practically irreversible**, so that the equilibrium constant could not be determined.

From the values of the equilibrium constants for the given reaction taken in conjunction with the values of the equilibrium constants for the formation of the corresponding hydrogen halide from hydrogen and the halogen, it is possible to find the value of the dissociation pressure of the halide in the metal and the halogen.

The same cobalt and nickel compounds, were already investigated before this in the same way as the studies of the equilibrium of the hydrogen reduction reaction by Jellinek and Uloth [2] ($CoCl_2$, $CoBr_2$, $NiCl_2$ and $NiBr_2$ by the dynamic method, 1926), by Berger and Crut [3] ($NiCl_2$ by the static method, 1921), by Crut [4] ($NiBr_2$, $CoCl_2$, $CoBr_2$ by the static method, 1924), and by Partington and Towndrow [5] ($CoCl_2$ by the static method, 1924). The data obtained by these authors were used to calculate the standard thermodynamic constants given in Britske and

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* Preliminary data on $CoCl_2$ and $CoBr_2$ were published in the Bulletin of the Leningrad State University, No. 26 (1950). These results are extended and amplified in the present paper.

** This is very important, as the literature contains instances when, in equilibrium studies, use was made of the reduction of such compounds by hydrogen which should be reduced practically irreversibly, and the observed gas composition was erroneously taken as the equilibrium value. For example, Jellinek used hydrogen reduction in the case of $CuCl_2$ and $CrCl_3$, and his data are quoted in tables.

Kapustinsky's [6] and Brewer's [7] tables.[*] However, we wished to repeat and amplify these studies, as the data in the literature are very incomplete. Crut's experiments (with the exception of $NiCl_2$) were carried out at only two temperatures, and with $CoCl_2$ only at one, which does not provide a sufficiently reliable basis for investigation of the temperature dependence of the constants. Partington and Towndrow made a fairly detailed investigation of the reduction of $CoCl_2$ (at 10° intervals) but the whole temperature range covered (400-500°) is narrow. Jellinek's data are available for three temperatures only, and, as will be shown later, these three points are not always in good agreement with each other. In addition, the dynamic method used by Jellinek (and by some other workers) for studying the equilibrium does not appear to be always reliable [9].

EXPERIMENTAL

Method of investigation

The circulation method was used for studying the equilibria. Its principle is, as is known, that the gas repeatedly passes over the substance studied, which is kept in a furnace at a definite temperature. Gas samples are analyzed at intervals and the results are used to determine when equilibrium is set up. The equilibrium was approached from two opposite directions. Agreement between the results was taken as proof that equilibrium had been attained.

The apparatus used for the study is shown diagramatically in Fig. 1, which shows the arrangement of the separate parts, where a) is the furnace, the temperature of which was kept constant to ±1°; b) is a piece of porcelain tube (instead of the usual boat) with the substance being reduced; c) is a Pt—Pt/Rh; thermocouple; d) are communicating vessels containing mercury for regulating the pressure in the system and for displacement of gas samples for analysis (usually the experiments were carried out at pressures 30-40 mm above atmospheric); e) is a circulating pump with mercury seals, which let gas through in one direction only; the movable bulb is moved up and down with the aid of a motor; f) is a manometer; g) is a three-way tap for taking gas samples; h) is an absorber for the hydrogen halide, filled with distilled water or with standard alkali solution; i) is a gas buret for measuring the volume of hydrogen; j) are tubes with P_2O_5; k) are columns with $CaCl_2$ and KOH; m) is a hydrogen reservoir; n) is an electrolytic cell; o) is a furnace with platinized asbestos; p) is a three-way tap for filling the system with hydrogen and for connecting it to the vacuum pump.

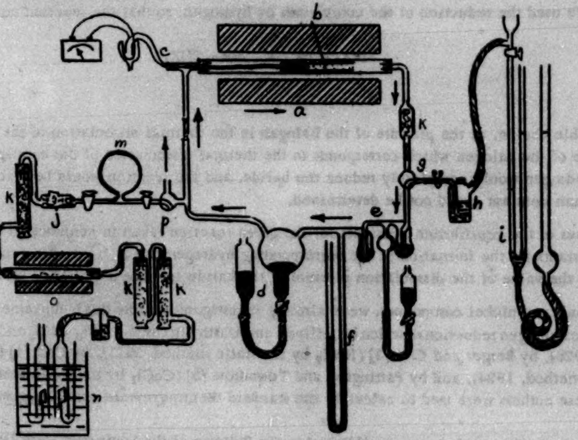

Fig. 1. Scheme of the circulation apparatus used for equilibrium studies.

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[*] After the completion of the present work, a paper was published by Busey and Giauque [8] in 1953, in which the reduction of $NiCl_2$ by hydrogen is described. The results obtained, as will be shown below, are in close agreement with ours.

When the reaction was conducted from the side of oxidation of the metal by hydrogen halide, excess of the latter in the gas mixture (in comparison with the equilibrium composition) was attained as follows: the substance studied, placed, as usual, in the furnace in a hydrogen atmosphere, was heated to 50-100° above the temperature of the experiment, with the pump working. When the desired composition of gas was reached, the temperature of the furnace was quickly lowered to the required level. In some experiments, if sufficient volume of gas still remained, after an experiment had been carried out at some temperature, the experiment was simply performed at a lower temperature. The total gas pressure in the system and the partial volumes of the two gases in the mixture (from analytical data) were used to calculate the partial pressure of each gas and the value of $\frac{p^2_{HX}}{P_{H_2}}$. After two consecutive samples taken at adequate time intervals gave equal results, the equilibrium could be considered as established; then the ratio $\frac{p^2_{HX}}{P_{H_2}}$ is equal to K_p.

TABLE 1

Substance	Vapor pressure at temperature (°C)		
	10^{-4} atm. (0.076 mm)	10^{-3} atm. (0.76 mm)	10^{-2} atm. (7.6 mm)
$CoCl_2$	507	612	672
$CoBr_2$	447	–	–
$NiCl_2$	589	661	748
$NiBr_2$	487	–	–

The value of the partial pressure of the halogen vapor can be neglected in calculations of the equilibrium constants in the present instance, as this value is negligibly small. According to Brewer's [7] approximate data, the vapor pressure has the values shown in Table 1.

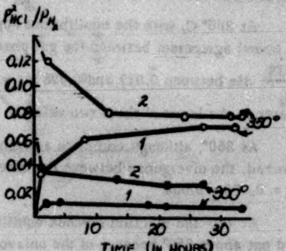

Fig. 2. Variation of gas composition with time (during approach to equilibrium) for the reaction $NiCl_2 + H_2 \rightleftharpoons Ni + 2HCl$ 1) Direct reaction, 2) reverse reaction.

According to Schäfer and Krehl [1], the vapor pressure for $CoCl_2$ is 0.64 mm at 652° and 4.4 mm at 707°.

Preparation of the samples.

Anhydrous $NiCl_2$ was prepared by decomposition of the hexamine ($NiCl_2 \cdot 6NH_3$) which was precipitated from a saturated nickel sulfate solution by an ammonia solution saturated with ammonium chloride. The washed and dried hexamine was heated for a long time at 200° for complete removal of ammonia [10].

Anhydrous $NiBr_2$ was prepared from nickel carbonate (which, according to spectrographic data, contained not more than 0.001% cobalt) by the action of hydrobromic acid. After evaporation and vacuum drying, the salt was dried in a stream of hydrogen mixed with hydrogen bromide at ~250° C. Analysis showed that the resulting substance contained from 1.5 to 2.5% metallic nickel, formed by reduction with hydrogen, but for our purposes this was unimportant.

Anhydrous $CoCl_2$ was prepared from commercial $CoCl_2 \cdot 6H_2O$ (chemically pure) by first drying it simply by heating in air, and then (when the nearly anhydrous salt became pale blue) in a stream of dry hydrogen chloride of about 250°.

Anhydrous $CoBr_2$ was prepared in the same way as nickel bromide, from cobalt carbonate (chemically pure).

As cobalt salts are extremely hydroscopic and could again absorb some moisture during transfer to the furnace, they must be finally dried in the apparatus itself by heating in a vacuum with the pump working.

The purity of all the original nickel and cobalt salts was previously checked by spectrum analysis*.

The equilibria in the reduction of $NiCl_2$, $NiBr_2$, $CoCl_2$ and $CoBr_2$ by hydrogen were mainly studied in the 300-600° temperature range. The upper limit of this range was sometimes determined by noticeable sublimation of the salt into a less hot part of the furnace, while the remaining salt was often completely, or nearly completely, reduced to the metal; in such cases erroneous values of K_p were obtained and often the hydrogen halide content in the samples fell appreciably. This was found, for example, at 655° for $NiBr_2$, and at 600° and especially at 700° for $CoBr_2$, when no equilibrium was attained at all. Sometimes the limits of the temperature range were determined by the composition of the gas at equilibrium; if the content of one of the gases is only a few percent of the total gas mixture, then a small error in analysis leads to a large error in the value of $\frac{P^2_{HX}}{P_{H_2}}$. The lower limit of the temperature range, apart from the reason given, was usually determined by the kinetics of the process. Below 300° the reaction rate was usually so low that although the reaction still proceeded, the process did not reach equilibrium.

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* The spectrum analysis was performed by M. M. Kler.

The equilibrium in the reduction of nickel chloride by hydrogen was studied * at 300, 350, 420, 450, 470, 500 and 550° C.

At 300° C, with the equilibrium approached from two opposite directions, despite the long time used (up to 33 hours) agreement between the gas phase compositions could not be reached (see Fig. 2). The values found for $\frac{P^2_{HX}}{P_{H_2}}$ lie between 0.011 and 0.028 (as will be seen later, the true value of the equilibrium constant is apparently nearer to the lower of these two values).

At 350°, although complete agreement between the results during the approach to equilibrium again was not reached, the divergence between the curves was already much less (Fig. 2) and the average value taken was $K_p = 0.078 \pm 0.004$.

At 420° the reaction reached equilibrium in 6-10 hours. The experiments with nickel chloride were not carried out above 550° because of the unfavorable gas composition ratio and of the appreciable sublimation of the salt.

Table 2 shows all the experimentally determined and assumed values (average, or chosen from the course of the lines in the graphs) for K_p and the volume composition of the gas at equilibrium.* *

The results of the investigation of equilibria in the reduction of $NiBr_2$, $CoCl_2$, and $CoBr_2$ are shown in Tables 3, 4 and 5.

DISCUSSION OF RESULTS

An examination of the values obtained for K_p shows that the chlorides of cobalt and nickel are more easily reduced by hydrogen than the bromides (the values of K_p are higher for the chlorides, and appreciable reduction begins at lower temperatures) despite the high thermal stability of the chlorides and the fact that the entropy increase during the reduction is rather less for the chlorides than for the bromides. This is generally true for the great majority of chlorides and bromides and is explained by the much greater heat of formation of HCl in comparison with HBr, which makes the reduction of chlorides less endothermic than that of bromides.

A comparison of Co and Ni compounds with the same halogen shows that cobalt chloride and bromide are more difficult to reduce by hydrogen than the nickel compounds, although the difference in their heats of formation is very small (it is a little greater for cobalt than for nickel halides), and therefore there is little difference in the heat effects of their reduction reactions. Differences in the entropies of cobalt and nickel halides are decisive here.

No heat capacity data (with the exception of $NiCl_2$ [11]) are available for exact calculations of the thermodynamic functions of the compounds studied, and therefore the usual approximate calculation method was used, which, nevertheless, gives a comparative picture on the basis of which certain conclusions in relation to the periodic system may be drawn.

The values of the equilibrium constants for the reduction of halides by hydrogen were used to calculate, by means of the formula $\Delta F = -RT\ln K_p$, the values for the changes of free energy during the reactions, shown in Tables 2-5. When $\log K_p$ is plotted against $1/T$, the values of $\log K_p$ lie almost exactly on straight lines (this sometimes formed the basis of acceptance for the values of K_p if the experimental results fluctuated) (Figs. 3 and 4).

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* With the participation of K. S. Kasimov.

* * The arrows ↑ and ↓ indicate the direction of the reaction during the approach to equilibrium. The sign ↑ represents the reaction $MeX_2 + H_2 = Me + 2HX$, and the sign ↓, the reaction $Me + 2HX = MeX_2 + H_2$. The data in brackets cannot be considered as sufficiently accurate.

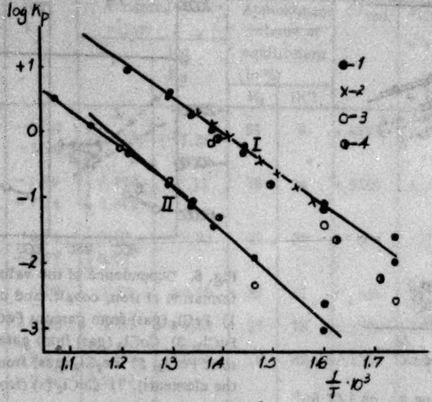

Fig. 3. Dependence of log K_p on $\frac{1}{T}$ for the reduction of nickel chloride and bromide by hydrogen.
I) $NiCl_2 + H_2 \rightleftharpoons Ni + 2HCl$, II) $NiBr_2 + H_2 \rightleftharpoons Ni + 2HBr$.
1) Our data, 2) Busey and Giauque, 3) Jellinek et al, 4) Crut.

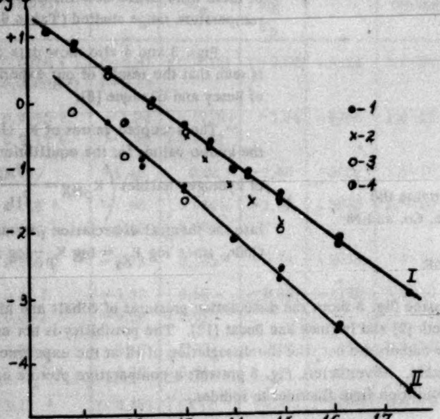

Fig. 4. Dependence of log K_p on $\frac{1}{T}$ for the reduction of cobalt chloride and bromide by hydrogen.
I) $CoCl_2 + H_2 \rightleftharpoons Co + 2HCl$, II) $CoBr_2 + H_2 \rightleftharpoons Co + 2HBr$.
1) Our data, 2) Partington, 3) Jellinek et al., 4) Crut.

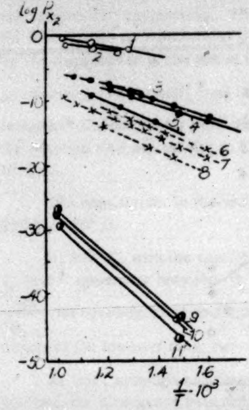

Fig. 5. Dependence of log P_{X_2} on 1/T for the halides of iron, cobalt, and nickel.
1) NiI_2, 2) CoI_2, 3) $NiBr_2$, 4) $CoBr_2$, 5) $FeBr_2$, 6) $NiCl_2$, 7) $CoCl_2$, 8) $FeCl_2$, 9) NiF_2, 10) CoF_2, 11) FeF_2.

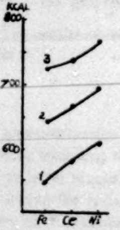

Fig. 7. Factors which determine the enthalpy of formation of Fe, Co, and Ni dichlorides.
1) ΣI, 2) $\Sigma I + s$, 3) E + const.

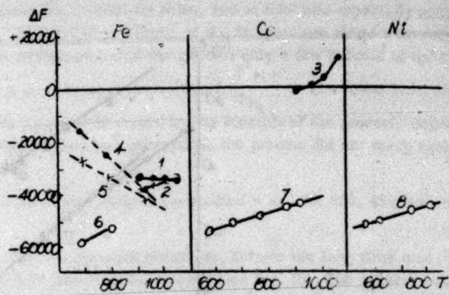

Fig. 6. Dependence of the values of ΔF on temperature for the formation of iron, cobalt, and nickel chlorides.
1) $FeCl_3$ (gas) from gaseous $FeCl_2$, 2) Fe_2Cl_6 (gas) from gaseous $FeCl_2$, 3) $CoCl_3$ (gas) from gaseous $CoCl_2$, 4) $FeCl_3$ (gas) from solid $FeCl_2$, 5) Fe_2Cl_6 (gas) from solid $FeCl_2$, 6) $FeCl_2$ (s) (from the elements), 7) $CoCl_2$ (s) (from the elements), 8) $NiCl_2$ (s) (from the elements).

Because of the linear nature of this relationship, it was assumed as an approximation that, in the temperature range investigated, the entropy (ΔS) and enthalpy (ΔH) values for the reactions are independent of the temperature, and the mean values of these were hence determined for the reduction reaction in the temperature range studied (Table 6).

Figs. 3 and 4 also show data obtained by other authors. It is seen that the results of our experiments agree closely with those of Busey and Giauque [8].

The accepted values of K_p (for the reduction reaction) and the known values for the equilibrium constants for the formation of hydrogen halides $\left(K_{pHX} = \frac{P^2_{HX}}{P_{H_2} \cdot P_{X_2}}\right)$ were used to calculate the thermal dissociation pressures of $NiCl_2$, $NiBr_2$, $CoCl_2$ and $CoBr_2$, since $\log P_{X_2} = \log K_p - \log K_{pHX}$ (Fig. 5 and Tables 2-5).

For comparison, the same Fig. 5 shows the dissociation pressures of cobalt and nickel fluorides and iodides from the data of Jellinek and Uloth [2] and Jellinek and Rudat [12]. The possibility is not excluded that these results are incorrect for iodides, as the authors did not take the dissociation of HI at the experimental temperature into account, but no other data are available. Nevertheless, Fig. 5 presents a comparative picture of the variation of the thermal stability of halides in the transition from fluorides to iodides.

The values of log P_{X_2} were also used to find the free energies of formation of the corresponding halides, and then the approximate values of ΔF_{298} and also approximate mean values of ΔH of formation and ΔS of formation for the temperature range studied. The values obtained are shown in Table 6.

It may be seen by an examination of the experimental results that nickel bromide at a little above 500° shows a small break in the log K_p line and correspondingly in the log P_{Br_2} line. Although the equilibrium data at these temperatures are less reliable, it was still reasonable to assume that this effect is explained by a transition to another modification. To verify this assumption, x-ray photographs were taken of nickel bromide specimens; 1) dried in a vacuum at 250°, and 2) held in a vacuum (for 5-6 hours) at ~600°. Chemical analysis gave the same results for both specimens, corresponding to the composition $NiBr_2$. The x-ray diagrams confirmed the existence of different structures.

TABLE 2

Nickel chloride

Temperature		$\frac{1}{T}\cdot 10^3$	K_p (experimental)	log K_p	Accepted values		Approximate volume at equilibrium (in %)		$\Delta F_{red.}$	P_{Cl_2} (in atm.)	log P_{Cl_2}	$\Delta F_{form.}$ (in cal.)
°C	°K				K_p	log K_p	H_2	HCl				
300	573	1.745	0.028↓ 0.011↑	−1.55 −1.96	(0.013)	(−1.88)	91	9	+ 4929	$2.6\cdot 10^{-20}$	−19.59	−51360
350	623	1.605	0.082↓ 0.073↑	−1.09 −1.14	0.078 ± 0.005	−1.11	76	24	+ 3163	$3.4\cdot 10^{-18}$	−17.47	−49780
420	693	1.443	0.58↓ 0.60↑	−0.24 −0.22	0.59 ± 0.01	−0.23	47	53	+ 697	$1.0\cdot 10^{-15}$	−15.00	−47530
450	723	1.383	1.23↑	+ 0.09	1.23	+ 0.09	39	61	− 330	$8.0\cdot 10^{-15}$	−14.10	−46630
470	743	1.346	2.00↑	+ 0.30	2.00	+ 0.30	27	73	−1020	$2.8\cdot 10^{-14}$	−13.55	−46060
500	773	1.293	4.04↑ 3.9 ↓	+ 0.61 + 0.59	4.00 ± 0.07	+ 0.60	18	82	−2129	$1.8\cdot 10^{-13}$	−12.74	−45060
550	823	1.215	(9.8)	(+ 0.99)	(9.8)	(+ 0.99)	9	91	(−3703)	$(2\cdot 10^{-12})$	(−11.71)	−(44170)

TABLE 3

Nickel bromide

Temperature		$\frac{1}{T}\cdot 10^3$	K_p(experimental)	log K_p	Accepted values		$\Delta F_{red.}$	P_{Br_2} (in atm.)	log P_{Br_2}	$\Delta F_{form.}$ (in cal.)
°C	°K				K_p	log K_p				
350	623	1.605	(0.0016 ↓) (0.00098 ↑)	(−2.6) (−3.04)	(0.0012)	(−2.92)	+ 8324	$3.0\cdot 10^{-13}$	−12.52	−35690
410	683	1.463	0.0115 ↑ 0.0117 ↓	−1.94 −1.93	0.0116 ± 0.0001	−1.94	+ 6061	$1.6\cdot 10^{-11}$	−10.79	−33720
450	723	1.383	0.040	−1.40	0.04	−1.40	± 4630	$1.5\cdot 10^{-10}$	− 9.81	−32450
475	748	1.335	0.088 ↑ 0.084 ↓	−1.06 −1.08	0.084 ± 0.004	−1.08	+ 3696	$5.7\cdot 10^{-10}$	− 9.24	−31550
500	773	1.294	0.165 ↑	−0.78	0.165	−0.78	+ 2758	$1.9\cdot 10^{-9}$	− 8.71	−30800
550	823	1.215	0.50 ↑ 0.51 ↓	−0.30 −0.29	0.50 ± 0.01	−0.30	+ 1129	$1.6\cdot 10^{-8}$	− 7.80	−29370
600	873	1.146	1.33 ↓ 1.32 ↑	+ 0.12 + 0.12	1.33 ± 0.01	+ 0.12	− 479	$9.8\cdot 10^{-8}$	− 7.01	−28000
655	928	1.077	(3.1) ↑ (2.84) ↑	(+ 0.49) (+ 0.45)	(3.1)	(0.49)	−2080	$5.4\cdot 10^{-7}$	− 6.27	−26620

The changes in the slopes of the log $K/\frac{1}{T}$ and log $P_{Br_2}/\frac{1}{T}$ lines were used to calculate the value of the enthalpy for the transition from one modification to the other; this was found to be about 5.8 kcal. The transition temperature was not determined exactly, but according to the graph it is ~520° C.

An exactly similar investigation was carried out with cobalt bromide. Here the x-ray diagrams were the same, so that there was no structural change.

TABLE 4

Cobalt chloride

Temperature °C	Temperature °K	$\frac{1}{T}\cdot 10^3$	K_p(experimental)	log K_p	Accepted values K_p	Accepted values log K_p	$\Delta F_{red.}$	P_{Cl_2} (in atm.)	log P_{Cl_2}	$\Delta F_{form.}$ (in cal).
300	573	1.745	(0.0012)	(−2.93)	(0.0011)	(−2.95)	+7734	$2.2\cdot 10^{-21}$	−20.66	−54180
350	623	1.605	0.0071	−2.15	0.0069 ± ± 0.0007	−2.16	+6158	$3.0\cdot 10^{-19}$	−18.52	−52730
			0.0066	−2.18						
			0.0076	−2.12						
400	673	1.486	0.035 ↑	−1.45	0.034 ± ± 0.004	−1.47	+4495	$2.1\cdot 10^{-17}$	−16.67	−51300
			0.036 ↑	−1.44						
			0.030 ↓	−1.52						
430	703	1.422	0.085 ↓	−1.07	0.081 ± ± 0.004	−1.09	+3505	$2.0\cdot 10^{-16}$	−15.70	−50510
			0.083 ↑	−1.08						
			0.079 ↓	−1.10						
			0.075 ↑	−1.12						
470	743	1.346	0.21 ↓	−0.67	0.21 ± ± 0.02	−0.67	+2278	$3.2\cdot 10^{-15}$	−14.50	−49330
			0.21 ↑	−0.67						
			0.22 ↑	−0.66						
			0.24 ↓	−0.62						
500	773	1.294	0.42 ↓	−0.37	0.44 ± ± 0.02	−0.36	+1273	$2.0\cdot 10^{-14}$	−13.70	−48450
			0.44 ↑	−0.36						
			0.45 ↑	−0.34						
540	813	1.230	1.00 ↑	0.00	1.03 ± ± 0.04	+0.01	−37	$2.0\cdot 10^{-13}$	−12.69	−47210
			1.07 ↑	+0.03						
600	873	1.147	3.2	+0.5	3.2	+0.5	−1997	$4.0\cdot 10^{-12}$	−11.40	−45530
650	923	1.083	(7.73)	+0.89	(7.3)	(+0.86)	(−3632)	$(3.7\cdot 10^{-11})$	(−10.43)	−44030
			(6.8)	(0.83)						
700	973	1.028	(13.1)	(+1.12)	~13	(+1.12)	(~−4885)	$(2.3\cdot 10^{-10})$	(− 9.63)	

TABLE 5

Cobalt bromide

Temperature °C	Temperature °K	$\frac{1}{T} \cdot 10^{-3}$	K_p (experimental)	log K_p	Accepted values K_p	Accepted values log K_p	$\Delta F_{red.}$	P_{Br_2} (in atm.)	log P_{Br_2}	$\Delta F_{form.}$ (in cal.)
300	573	1.745	(0.000007)	(−5.29)	(~ 0.00003)	(~ −4.5)	–	–	–	–
			(0.00003)	(−4.52)						
			(0.00009)	(−4.03)						
350	623	1.605	0.00033 ↓	−3.49	0.00032 ± 0.00002	−3.5	+9977	$7.9 \cdot 10^{-14}$	−13.10	−37350
			0.00031 ↑	−3.51						
			0.00028 ↓	−3.55						
400	673	1.485	0.0026 ↓	−2.58	0.0021 ± 0.0004	−2.67	+8221	$2.3 \cdot 10^{-12}$	−11.63	−35810
			0.0019 ↓	−2.72						
500	773	1.294	0.047 ↓	−1.33	0.047 ± 0.001	−1.33	+4704	$5.4 \cdot 10^{-10}$	− 9.26	−32750
			0.047 ↑	−1.33						
			0.044 ↑	−1.36						
550	823	1.215	0.11	−0.96	(0.16)	(−0.8)	+3012	$(5.0 \cdot 10^{-9})$	(− 8.3)	(−31250)
			0.12	−0.92						
600	873	1.147	(0.50) ↑	(−0.3)	(0.5)	(−0.3)				

TABLE 6

Substance	T (° K)	$MeX_2 + H_2 = Me + 2HX$		$Me + X_2 = MeX_2$		
		$\Delta H_{red.}$ (in kcal.)	$\Delta S_{red.}$ (in entropy units)	$\Delta H_{form.}$ (in kcal.)	$\Delta S_{form.}$ (in entropy units)	ΔF_{298} (in kcal.)
$NiCl_2$	573-823	+ 25.14	+ 35.2	−69.5	−31.5	−60.01
$NiBr_2$	623-790	+ 31.14	+ 36.7	−55.84	−32.45	−46.20
$NiBr_2$	790-928	−	−	~−50	−	−
$CoCl_2$	573-743	+ 26.44	+ 32.6	−71.0	−29	−62.34
$CoBr_2$	573-873	+ 31.88	+ 35.15	−56.4	−30.6	−47.31

TABLE 7

Reaction	ΔS for the reaction
$2FeCl_2$ (S) + Cl_2 + 46.2 kcal. = $2FeCl_3$ (gas)	+ 90
$2FeCl_2$ (S) + Cl_2 + 13.6 kcal. = Fe_2Cl_6 (gas)	+ 59
$2FeCl_2$ (gas) + Cl_2 − 29.8 kcal. = $2FeCl_3$ (gas)	+ 4.8
$2FeCl_2$ (gas) + Cl_2 − 62.4 kcal. = Fe_2Cl_6 (gas)	− 26.4
$2CoCl_2$ (gas) + Cl_2 − 33.8 kcal. = $2CoCl_3$ (gas)	− 36.3

TABLE 8

Temperature ° K	ΔF (in cal.)		
	$2FeCl_2$ (gas) + Cl_2 = = Fe_2Cl_6 (gas)	$2FeCl_2$ (gas) + Cl_2 = = $2FeCl_3$ (gas)	$2CoCl_2$ (gas) + Cl_2 = = $2CoCl_3$ (gas)
918	−38100	−34210	− 631
971	−36700	−34460	+ 1191
1019	−35300	−34680	+ 3477
1073	−33970	−34950	+ 11420

TABLE 9

Temperature ° K	ΔF (in cal.)	
	$2FeCl_2$ (s) + Cl_2 = $FeCl_6$ (gas)	$2FeCl_2$ (s) + Cl_2 = $2FeCl_3$ (gas)
700	−27700	−16800
800	−33600	−25800
940	−41840	−38400

TABLE 10

Element	s	ΣI	ΣI + s	The difference ΣI + s for adjacent elements	E for $MeCl_2$	Difference of E for adjacent elements	E + const.	ΔH
Fe	96.7	545.8	642.5	23.7	607.5	13.5	724.5	82
Co	85	581.2	666.2	28	621	26.6	738	72
Ni	85	609	694		647.6		764.6	70.6

Our mean values for the enthalpy of formation could only be used in the case of $NiCl_2$ to find ΔH_{298}, as the necessary heat capacity data are available in that instance. For $NiCl_2$ Coughlin's [11] data were used, and for Ni, the specific heat equations:

$$C_p = 4.26 + 6.40 \cdot 10^{-3}\,T\ (273\text{-}626^\circ\ K),$$
$$C_p = 6.99 + 0.905 \cdot 10^{-3}\,T\ (626\text{-}1725^\circ\ K)\ [6],$$

the heat of transition of nickel was taken as 92 cal.; for chlorine, the data of Giauque and Overstreet [6] were used.

Recalculation of our mean value of ΔH from 700° K (the middle of the temperature range studied) to 298° K gave the value $\Delta H_{298} = 70.5$ kcal.

Comparison of iron, cobalt, and nickel halides

In conclusion, it was of interest to make some comparisons between the iron, cobalt, and nickel compounds with the use of our results and of the data available in the literature.

For a comparison of the probability of formation of trivalent iron, cobalt, and nickel halides we will confine ourselves to an examination of the chlorides. The fact that the compounds $CoCl_3$ and $NiCl_3$ cannot be expected to be stable can be concluded in advance from an examination of the values of the third ionization potentials of Fe, Co, and Ni.

As was shown by Shchukarev and Oranskaya [13], the values of the dissociation pressures of halides during consecutive transition from one element to another (for the elements of the first sub-period) change symbatically with the values of the ionization potentials, and in the present instance with the value of the third ionization potential, since the reaction $2MeCl_3 \rightleftharpoons 2MeCl_2 + Cl_2$ is involved. These have the following values [14].

	Mn	Fe	Co	Ni
I_3 kcal/g-atom	782	727	772	825

For solid $FeCl_3$, according to Kangro and Petersen [15] the dissociation pressure at 300° is about 50 mm. Solid $CoCl_3$ should be less stable, and its stability should be near to that of $MnCl_3$ (Co and Mn have similar values of I_3), and $NiCl_3$ is obviously still less stable. So far these compounds have not been obtained in the solid state. The formation of $CoCl_3$ and $MnCl_3$ in the gaseous state was detected by the action of excess chlorine on $MeCl_2$ vapors. Ferric chloride is stable both in the solid and in the gaseous states, and the gaseous state is represented by the equilibrium:

$$2FeCl_3\,(gas) - 32.55\ \text{kcal.} \rightleftharpoons Fe_2Cl_6\,(gas).$$

The equilibrium constants for this reaction were calculated by Schäfer [16] by an indirect method and later determined by Kangro and Bernstorff [17] by a static method in the temperature range 487-741° C. Their results show that at lower temperatures dimer molecules predominate, and as the temperature rises the equilibrium shifts in the direction of the monomer (at a total pressure of 100 mm and at ~800° C almost complete decomposition into the monomer takes place).

To determine the probability of reactions leading to the formation of trivalent Co and Ni halides, an attempt was made to compare the values of the free energy of the reactions of formation of these compounds, that is, for the reactions:

$$2MeCl_2 + Cl_2 \longrightarrow 2MeCl_3.$$

For the chlorides of iron, the data of Schäfer [18] and of Kangro and Bernstorff [17] were used, and for cobalt chloride, the data of Schäfer and Krehl [1], to calculate the values of ΔF for the reactions shown in Table 7.

The individual entropy values required for the calculation of ΔS for these reactions were taken as (in entropy units): Fe_2Cl_6 (gas), 171, from Schäfer [18]; $FeCl_2$ (gas)72.1 from Britske and Kapustinsky [6]; Cl_2 (gas), 53.3, from Britske and Kapustinsky [6]; $FeCl_3$ (gas), 101, our calculation from the data of Kangro and Bernstorff [17] and Schäfer [18]; $FeCl_3$ (s) 29.4, from Britske and Kapustinksy [6].

The values of ΔF given in Tables 8 and 9 were calculated on the assumption that ΔH and ΔS for the reactions are independent of temperature in the temperature range considered. For solid $FeCl_2$ the calculation was made to approximate the melting point of this compound (674°).

For the reactions between gaseous $MeCl_2$ and chlorine we selected, for convenient comparison, the temperature range for which Schäfer and Krehl's experimental data for $CoCl_3$ are available; in absence of other data we assumed, like these authors, that $CoCl_3$ itself and not the dimer is formed (which is not certain at present).

For the reactions of formation of solid $MeCl_2$ from the metals and chlorine, our data (Tables 2, 4) were used for $CoCl_2$ and $NiCl_2$, and the data of Shchukarev, Oranskaya, and Novikov [19] for $FeCl_2$.

The values of ΔF so obtained (Tables 2, 4, 8, and 9) were used to plot the ΔF-temperature curves (Fig. 6). Fig. 6 shows that in the case of iron the values of free energy for the formation both of $FeCl_3$ (gas) (1) and Fe_2Cl_6 (gas) (2) from gaseous $FeCl_2$ are far below zero, and the reaction of Fe_2Cl_6 formation is at first the more favorable; at about 770° the curves for these processes intersect.

For $CoCl_3$ (gas) the Curve (3) lies almost entirely in the region of positive ΔF values. If we assume that not $CoCl_3$ but the dimer is formed, the position of the curve would, of course, change, but apparently it would remain in the same region. Thus, a comparison of the curves shows that $CoCl_3$ should be much less stable than $FeCl_3$

The reactions for the formation of $FeCl_3$ (gas) (4) and Fe_2Cl_6 (gas) (5, Fig. 6) from solid $FeCl_2$ are endothermic, but as they are accompanied by large entropy increases (and therefore the ΔF curves for these reactions are very steep) at sufficiently high temperatures they can compete with the reactions of gaseous $FeCl_2$.

The reaction $2CoCl_2(s) + Cl_2 + 76.4$ kcal. $= 2CoCl_3$ (gas) is highly endothermic, which is due to the high heat of sublimation of $CoCl_2$ (55 kcal., according to Schäfer and Krehl [1]). For the calculation of the free energy of this reaction, no data are available for the entropy of cobalt chlorides. Tentatively assumed values (by analogy with the iron compounds) give results which are too inaccurate, and are not reproduced here; it appears, however, that the ΔF values lie in the highly positive region (of the order of 20-40 kcal.).

$NiCl_3$ should be even less stable than $CoCl_3$, but its formation may be assumed possible at high pressures of chlorine.

The values of ΔF for the formation of solid $FeCl_2$ (6), $CoCl_2$ (7), $NiCl_2$ (8) all lie far down on the graph, which is in agreement with the stability of these compounds.

The bromides and iodides are as a rule, less stable than the chlorides; therefore they obviously cannot be obtained for trivalent Co and Ni. The formation of NiF_3 may be presumed, although it is still unknown.

In a comparison of Fe, Co, and Ni compounds it is interesting to attempt to find a reason for the great similarity between cobalt and nickel and their difference from iron. If the values of the enthalpy of formation of a large number of binary compounds of these three elements are examined, it is seen that they are always very similar for analogous Co and Ni compounds, and generally differ by less than 2 kcal., while the difference between the enthalpies of formation of iron compounds and the enthalpies of formation of the same cobalt compounds are several kilocalories.

The enthalpy of formation of bivalent methal halides may be given by the following equation:

$$\Delta H = (E + 2e - (D + \Sigma I + s),$$

where E is the lattice energy, e is the halogen electron affinity, D is the dissociation energy of 1 mole of the halogen, ΣI is the sum of the 1st and 2nd dissociation potentials, and s is the energy of sublimation of the metal.

For the same halogen, $2e - D =$ const, and the difference between the values of ΔH for the halides of the three elements in question will depend on the difference $E - (\Sigma I + s)$.

The data in Table 10 for compounds of the type $MeCl_2$ for Fe, Co, and Ni, show that only the values of the energy of sublimation for Co and Ni are equal [6], and for iron it is somewhat greater, while the other values which determine the value of ΔH are not near each other for cobalt and nickel, and as a result the values of E and $(\Sigma I + s)$ differ even more for Ni and Co than for Co and Fe.

However, the difference between changes in the values of E and the values of $\Sigma I + s$ is almost the same in the transition from cobalt to nickel, which leads to similar values of ΔH, while for iron this difference is not the same. This is clearly shown in Fig. 7, which shows the curves for the values (for the chlorides) of ΣI, $(\Sigma I + \underline{s})$ and $[E + (2e - D)] = E + \text{const}$ for iron, cobalt, and nickel. The regions of the curves (E + const) and $\Sigma I + \underline{s}$ from Co to Ni lie almost parallel (which is in agreement with the almost equal values of ΔH) but in the transition to iron the E + const curve has a small inflexion, due to the smaller fall in the value of E in the transition from Fe to Co than from Co to Ni, which corresponds to a greater value of ΔH.

SUMMARY

1. The circulation method was used to determine the equilibrium of the reduction of $NiCl_2$, $NiBr_2$, $CoCl_2$ and $CoBr_2$ by hydrogen in the temperature ranges: $NiCl_2$ 300-550° C, $NiBr_2$ 350-655° C, $CoCl_2$ 300-650° C, $CoBr_2$ 300-600° C.

2. The values found for the equilibrium constants lead to the following conclusions: a) both cobalt and nickel chlorides are more easily reduced by hydrogen than the bromides, despite the higher thermal stability of the chlorides; b) a comparison of compounds of Co and Ni with the same halogen showed that cobalt halides are reduced less easily by hydrogen than nickel halides, and since the thermal stabilities of these compounds are almost the same, the entropy factor plays the decisive role.

3. The values found for the equilibrium constants for the reduction of $NiCl_2$, $NiBr_2$, $CoCl_2$ and $CoBr_2$ by hydrogen were used to find the values for the free energy changes in these reactions, and also the mean values of the enthalpy and entropy of the reduction reactions.

4. The values found for the equilibrium constants for the reduction reactions were used to calculate the thermal dissociation pressures of $NiCl_2$, $NiBr_2$, $CoCl_2$ and $CoBr_2$ and also the changes of free energy in the formation of these halides from the elements and the mean values for the enthalpy and entropy of formation of these compounds.

5. By an examination of the values of the free energy changes in the formation of chlorides of bi- and trivalent Fe, Co, and Ni it is shown that the stability of the trivalent halides decreases from Fe to Ni.

6. An attempt was made to find why, despite the different values of the ionization potentials of Fe, Co, and Ni and of the crystal lattice energies of compounds of these elements, the enthalpies of formation of cobalt and nickel compounds are almost the same, but differ from the enthalpy of formation of iron compounds. The reason is apparently the irregular variation of the crystal lattice energy in the transition Fe $\longrightarrow$ Co $\longrightarrow$ Ni.

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THE ROLE OF IONIZATION POTENTIALS IN THE THERMODYNAMICS OF THE HALIDES OF METALS IN THE FIRST SUB-PERIOD OF THE FOURTH PERIOD OF D. I. MENDELEEV'S SYSTEM

S. A. Shchukarev and M. A. Oranskaya

It is interesting to determine the causes which affect the possibility of the existence of a given element in a particular degree of oxidation. The obvious way of solving the problem is to refer to the periodic law and to compare the thermal stabilities of the compounds of some definite class, for example, the chlorides of the elements of the first sub-period of the fourth period in Mendeleev's system. The reason for the choice of the chlorides of these elements was that the greatest amount of experimental data is available in the literature for them [1]. The dissociation pressure of a compound is taken as a measure of its thermal stability. A compound can exist under normal pressures if its dissociation pressure at a given temperature is less than 1 atm., and the compound decomposes if this pressure exceeds 1 atm.*.

The following chlorides of the first sub-period have been obtained:

–	–	–	–	–	–	–	–	$CuCl$	–
–	$TiCl_2$	VCl_2	$CrCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$CuCl_2$	$ZnCl_2$
$ScCl_3$	$TiCl_3$	VCl_3	$CrCl_3$	$MnCl_3$	$FeCl_3$	$CoCl_3$	–	–	–
–	$TiCl_4$	VCl_4	$CrCl_4$	–	–	–	–	–	–

We first examine the dihalides. The values for the dissociation pressures of $FeCl_2$ [2], $CoCl_2$, $NiCl_2$ [3] and $CuCl_2$ were determined [4] by us, those for $ZnCl_2$ and VCl_2 were calculated from Brewer's tables [1], for $CrCl_2$ the data of Sano [5] and Doerner [6], and for $MnCl_2$ the data of Sano [7] were used. Table 1 shows the logarithms of the dissociation pressures of all these compounds (for their dissociation into the metal and chlorine) at various temperatures.

In Fig. 1, the logarithms of the dissociation pressure (at 400°) are taken along the ordinate axis, and calcium and the elements of the first sub-period are plotted along the abscissa axis. It is seen that the dissociation pressure gradually increases with the atomic number, but it has minimum values for $MnCl_2$ and $ZnCl_2$. The same figure shows the enthalpies of decomposition for these compounds.** As was to be expected, the enthalpy change from one element to another is antibatic to the change of the dissociation pressure, so that a low enthalpy of decomposition corresponds to a high dissociation pressure ($CuCl_2$), and, conversely, a high enthalpy of decomposition corresponds to a low dissociation pressure ($TiCl_2$, VCl_2, $MnCl_2$).

The course of the dissociation pressure curve plotted against the atomic number of the element should depend on values which characterize the cation, since the anion remains the same. Such values are, primarily, the sublimation energy of the metal and the first and second ionization potentials. Fig. 2 shows the variations of the sublimation energy (1), and of the first (2) and the second (3) ionization potentials, and of the sum of all these three, (5), with the atomic number of the element. Fig. 2 shows that only the curve for the second ionization potential (3) reproduces the curve for the dissociation pressure, and the resemblance between the curves becomes still more complete if the sum of the two potentials and the sublimation energy is taken (5), but the principal part is still played by the second ionization potential, as the principal term. Consequently, the change in the dissociation pressure, or the change in the thermal stability of the compounds, is in the first instance determined by the value of the second ionization potential. How is such an influence of this particular factor to be explained?

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* The possibility of the existence of compounds at high pressures is not considered here.

** The enthalpies are quoted for standard conditions, because specific heats have not been determined for every chloride.

TABLE 1

Temperature °C	Logarithm of dissociation pressure • (log P)								
	$TiCl_2$	VCl_2	$CrCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$CuCl_2$	$ZnCl_2$
219	–	–	–	–	–	–	–	−13.0	–
320	–	–	–	–	–	–	–	−10.2	–
350	–	–	–	–	–	−18.5	−17.5	–	–
392	–	–	–	–	–	–	–	− 8.7	–
400	−32.7	−29.9	−22.9	−29.0	−19.3	−16.7	−15.7	− 8.5	−24.6
420	–	–	–	–	–	–	−15.0	− 8.1	–
423	–	–	–	–	−18.6	–	–	–	–
427	−31.1	−28.7	–	–	–	–	–	–	−23.0
450	–	–	–	–	–	–	−14.1	–	–
470	–	–	–	–	–	−14.5	−13.6	–	–
473	–	–	–	–	−17.1	–	–	–	–
496	–	–	–	–	−16.4	–	–	–	–
500	–	–	–	–	–	−13.7	−12.7	–	–
523	–	–	–	–	−15.6	–	–	–	–
527	−25.7	−24.1	–	–	–	–	–	–	–
540	–	–	–	–	–	−12.7	–	–	–
547	–	–	–	−22.9	–	–	–	–	–
550	–	–	–	–	–	–	−11.7	− 6.0	–
595	–	–	–	–	−13.8••	–	–	–	–
600	–	–	–	–	–	−11.4	–	–	–
627	−22.5	−20.5	–	−20.2	–	–	–	–	–
632	–	–	−16.2	–	–	–	–	–	–
650	–	–	–	–	–	−10.4	–	–	–
677	–	–	−15.2	–	–	–	–	–	–
700	–	–	–	–	–	− 9.6	–	–	–
702	–	–	–	–	−11.9	–	–	–	–
725	–	–	–	–	−11.5	–	–	–	–
727	−19.4	−17.9	–	–	–	–	–	–	−15.3
772	–	–	−13.3	–	–	–	–	–	–
800	–	–	–	–	−10.3	–	–	–	–
805	–	–	−12.7	–	–	–	–	–	–
827	−16.9	−15.6	–	–	–	–	–	–	−13.3
893	–	–	−11.3	–	–	–	–	–	–
925	–	–	–	–	− 9.0	–	–	–	–
1005	–	–	–	–	− 8.1	–	–	–	–
1075	–	–	− 8.7	–	–	–	–	–	–

• The dissociation pressure is in atmospheres throughout.

•• From 595° the dissociation pressure of $FeCl_2$ was calculated from the data of Sano [7] and Bagdasarijan [9].

If we calculate the crystal lattice energies of the compounds in question and plot them on a graph, we again obtain a curve which resembles the curve for the sum of the ionization potentials and the sublimation energy (Table 2, Fig. 3).

In Fig. 3, the Curves 1, 2, 3, show the course of the variation of the latice energies for the chlorides (1), bromides (2) and iodides (3) of the elements in the first sub-group.• To the lattice energy a value is added which is constant for the given class of compounds, $-D + 2e$, where D is the dissociation energy of the halogen and $\underline{e}$ is the

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• The values of the ionization potentials were taken from [10], and the sublimation energies and enthalpies of formation from [11] and [1]; the enthalpies for the bromides and iodides were calculated for the formation of these compounds from gaseous halogens. The dissociation energies and the halogen electron affinities were taken from [12].

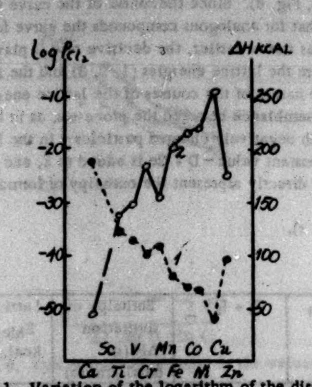

Fig. 1. Variation of the logarithm of the dissociation pressure of chlorides at 400°, and of the enthalpy of dissociation, in consecutive transition from Ca to Zn. 1) Enthalpy of dissociation, 2) logarithm of dissociation pressure.

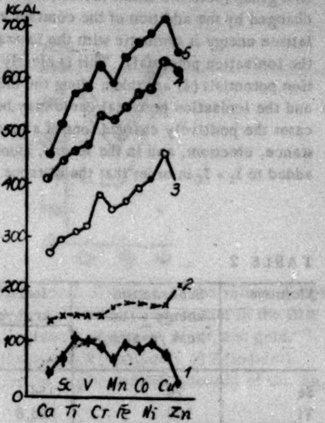

Fig. 2. Variation of the sublimation energy s (1), the first ionization potential I_1 (2), the second ionization potential I_2 (3), the sum of the two potentials $I_1 + I_2$ (4), and the sum of the ionization potentials and the sublimation energy $I_1 + I_2 + s$ (5) in consecutive transition from Ca to Zn.

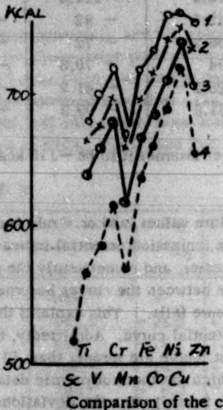

Fig. 3. Comparison of the changes of E + const. for halides with changes in the sum of the ionization potentials and sublimation energy for the elements of the first sub-period. 1) E + const. (chlorides), 2) E + const. (bromides), 3) E + const. (iodides), 4) $I_1 + I_2 + s$.

halogen electron affinity.* It is seen that the Curves 1, 2, 3 (Fig. 3) follow the course of the ionization potential curve, but their absolute values lie higher and they are flatter than the $\Sigma I + s$ curve (4). Such a resemblance between the curves may be seen not only for the halides of the elements of the first sub-period, but also for the compounds of these elements with the elements

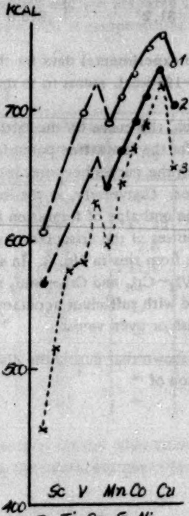

Fig. 4. Comparison of the changes of E + const. for oxides and sulfides with changes in the sum of the ionization potentials and sublimation energy for the elements of the first sub-period. 1) E + const. (oxides), 2) E + const. (sulfides), 3) $I_1 + I_2 + s$.

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* The significance of adding −D + 2e will be explained later.

of the sixth group (Fig. 4), and also for the compounds of the principal sub-groups, for example, the halides of the first group (both the alkali metals, Fig. 5, and the copper sub-group, Fig. 6). Since the course of the curve is not changed by the addition of the constant value, it may be assumed that for analogous compounds the curve for the lattice energy is symbatic with the ionization potential curve (as was stated earlier, the decisive role is played by the ionization potential). This is clearly seen in Figs. 5 and 6, where the lattice energies (1, 2, 3) and the ionization potentials (4) are taken along the ordinate axes. This symbatic nature of the courses of the lattice energy curve and the ionization potential curve may be attributed to a certain resemblance between the processes, as in both cases the positively charged ions of a given metal are combined with negatively charged particles — in the first instance, electrons, and in the second, anions. In Figs. 3 and 4 the constant value $-D + 2e$ is added to E, and $\underline{s}$ is added to $I_1 + I_2$ in order that the distance between the curves should directly represent the enthalpy of formation,

$$\Delta H = E + \text{const} - (\Sigma I + s).$$

TABLE 2

Element	Sublimation energy $\underline{s}$ (in kcal./g-atom)	Ionization potential (in kcal./g-atom)		$I_1 + I_2$	$I_1 + I_2 + \underline{s}$	Enthalpy of formation ΔH (in (kcal./mole)	Lattice energy E_{MeCl_2} (in kcal./mole)
		I_1	I_2				
Se	70	154.1	294.4	448.5	518.5	–	–
Ti	100	156.6	312.8	469.4	569.4	−125•	−577.4
V	85	155	348	503	588	−117	−588
Cr	89.3	154.1	377.4	531.5	620.9	−103.1	−607
Mn	69.7	170.4	333.5	503.9	573.6	−111.6	−568
Fe	96.7	180.1	365.7	545.8	642.5	− 82	−607.5
Co	85	179.4	401.8	581.2	666.2	− 72	−621
Ni	85	174.8	434.2	609	694	− 70.6	−647.6
Cu	81.2	176.4	467.4	644	725.2	− 41.2	−649.4
Zn	31.2	215.5	414.9	630.4	661.6	− 99.3	−643.9

• There are no experimental data for the heat of formation of $TiCl_2$. Brewer assumes it to be −115 kcal. by extrapolation, −125 kcal. seems to us more correct.

In all cases given, the curve for the lattice energy + const. is higher in absolute values, and as a rule is more flat, than the curve for the ionization potentials, from which it follows that as the ionization potential increases, the distance between the curves becomes less, that is, the ΔH of formation decreases, and consequently the dissociation pressure increases. Conversely, as the ionization potential falls, the distance between the curves becomes greater, and therefore the enthalpy of formation increases while the dissociation pressure falls. This explains the symbatic nature of the courses of the dissociation pressure curve and the ionization potential curve. Admittedly, there are some deviations from this in Fig. 3. In some regions portions of the E + const. curve are steeper than $\Sigma I + \underline{s}$. This is found in the VI_2—CrI_2 and CrI_2—MnI_2 regions, which are compounds for which the thermodynamic data have not been determined with sufficient accuracy, and it is possible that after further investigation the deviations from the rule will diminish or even vanish.

It can be shown that during the dissociation of compounds of metals of higher valency than two, for example, in the dissociation of

$$2MeCl_3 = 2MeCl_2 + Cl_2$$

or

$$2MeCl_4 = 2MeCl_3 + Cl_2,$$

the dissociation pressure will also vary with the third or fourth ionization potential. The dissociation pressures (at 400°) and enthalpies of the dissociation reactions of tri- and tetrachlorides are shown in Tables 3 and 4.

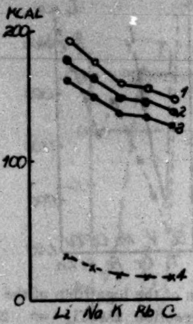

Fig. 5. Comparison of changes in the values of crystal lattice energies of halides with changes in the first ionization potential of alkali metals.
1) E (chlorides), 2) E (bromides), 3) E (iodides),
4) curve for the first ionization potential of the alkali metals.

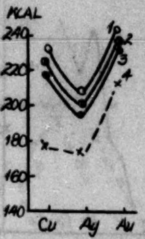

Fig. 6. Comparison of changes in the values of crystal lattice energies of halides with changes in the first ionization potential of copper, silver, and gold.
1) E (chlorides), 2) E (bromides), 3) E (iodides),
4) curve for the first ionization potential of Cu, Ag, and Au.

In Figs. 7 and 8 the ordinate axes show the logarithms of the dissociation pressures of $MeCl_3$ and $MeCl_4$, and also the values of the third and fourth dissociation potentials, and the abscissa axes give the elements of the first sub-period. It is seen that here, as for $MeCl_2$, the dissociation pressure curves and the ionization potential curves are symbatic. The dissociation pressure curve, like the third dissociation potential curve, has a maximum for $MnCl_3$ and a minimum for $FeCl_3$, and the ionization potential then rises. $CoCl_3$ in the solid state is extremely unstable and was prepared in 1952 by Schäfer and Krehl [14] only in the vapor state by the action of excess chlorine on $CoCl_2$ at temperatures above 645°. The existence of $NiCl_3$, $CuCl_3$, and $ZnCl_3$ is still less probable.

TABLE 3

Substance	I_3 (in kcal. / /g-atom)	log P_{Cl_2}	ΔH (in kcal./ /mole)	Literature source
$ScCl_3$	618	–	–	–
$TiCl_3$	652.5	−24.9	+100	–
VCl_3	696	−16.1	+ 86	–
$CrCl_3$	736	−14.5	+ 80	[6]
$MnCl_3$	782	+ 8.3	− 3	[1]
$FeCl_3$	727	+ 0.3	+ 28	[13]
$CoCl_3$	772	–	–	[14]•
$(NiCl_3)$	825	–	–	–
$(CuCl_3)$	916	–	–	–
$(ZnCl_3)$	919	–	–	–

TABLE 4

Substance	I_4(in kcal./ /g-atom)	log P_{Cl_2}	ΔH (in kcal / /mole)	Literature source
$ScCl_4$	1715	–	–	–
$TiCl_4$	1043	−10.95	+ 32.8	–
VCl_4	1113	− 2.6	+ 4	–
$CrCl_4$	1170	+ 11.9	−44	[6]
$(MnCl_4)$	1230	–	–	–
$(FeCl_4)$	1288	–	–	–
$(CoCl_4)$	1223	–	–	–
$(NiCl_4)$	1290	–	–	–
$(CuCl_4)$	1350	–	–	–
$(ZnCl_4)$	1420	–	–	–

• The data of Schäfer and Krehl [14] are not quite comparable with the data for the other trichlorides, as they prepared gaseous $CoCl_3$ from gaseous $CoCl_2$, while in the other instances the values are given for the dissociation of solid $MeCl_3$ into the halogen and solid $MeCl_2$.

The dissociation of $MeCl_4$ shows an ascending straight line only. The minimum on the ionization potential curve is found at Co, but Cr, which has a much lower ionization potential than Co, forms the very unstable compound $CrCl_4$, which can only be obtained in the solid state below −80° C [15], and therefore compounds of the type $MeCl_4$ are unlikely in elements beyond chromium.

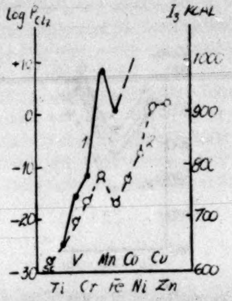

Fig. 7. Variation of the logarithm of the dissociation pressure for the reaction $2MeCl_3 \rightleftharpoons 2MeCl_2 + Cl_2$ at 400° C, and of the third ionization potential in the transition from Sc to Zn.
1) log P_{Cl_2}, 2) I_3.

TABLE 5

Halogen	Electron affinity e (kcal./g-atom	Dissociation energy D (kcal./mole)	2e−D
Fluorine	83	40	126
Chlorine	87	57	117
Bromine	81.6	45.2	118
Iodine	74.0	36.3	111.7

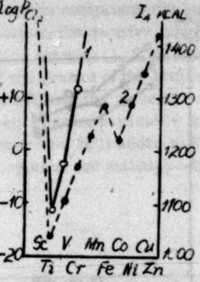

Fig. 8. Variation of the logarithm of the dissociation pressure for the reaction $2MeCl_4 \rightleftharpoons 2MeCl_3 + Cl_2$ at 400° C and of the fourth ionization potential in the transition from Sc to Zn.
1) log P_{Cl_2}, 2) I_4.

So far we have examined compounds of metals with the same halogen; if we now compare the thermal stabilities of different halides of the same metal, then we have for such compounds of bivalent metals:

$$\Delta H = E - D + 2e - \Sigma I - s.$$

The last two terms will be constant in the present instance. and the enthalpy of formation will depend on the lattice energy, dissociation energy of the halogen, and its electron affinity. The greater these three values are, the smaller will be the role of the constant subtracted from the lattice energy, the greater will be the enthalpy of formation, and the less will be the dissociation pressure. Table 5 gives the electron affinity and dissociation energy values for the halogens. The electron affinity and the dissociation energy of fluorine were taken as 83 kcal./g-atom and 40 kcal./mole [16].

Thus we see that the value 2e−D which is added to the lattice energy is greatest for fluorine, almost the same for chlorine as for bromine, and least for iodine, but these values do not greatly differ from each other (by not more than 14 kcal.). Therefore, the main influence on the value of the enthalpy of formation of the compounds should be exerted by the energy of the crystal lattice, which should increase as its component particles are able to approach closer to each other.

In compounds of the same metal the lattice energy will depend on the size of the halogen atoms. Fluorine will give compounds with the greatest lattice energy, and iodine, the least. The values which characterize the anion, 2e−D, as was already shown, change in the same direction; therefore the enthalpy of formation will be greatest for fluorides and least for iodides, while the dissociation pressure, which is a measure of the thermal stability of the compounds, will change in the opposite sense (Fig. 9, Table 6).

Fig. 9 shows logarithms of the dissociation pressures of different halides of the elements of the first sub-period at 400°. Parallel to the abscissa axis is a line a, which represents a dissociation pressure of 1 atmosphere. It is seen that while the dissociation pressures of fluorides lie well below the line a, the dissociation pressures increase in the transition to iodides, and for iodides the curves lie near the line a. The normal order of dissociation pressures for compounds of different valencies of the same element is such that compounds of lowest valency have the lowest pressure, and those of the highest valency, the greatest pressure. * Thus fluorides can form compounds in which the

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* In the event of a disproportionation reaction the order of pressures is disturbed.

element exhibits its highest valency; in iodides even compounds of the lowest valency are unstable, while compounds of the highest valency cannot exist at 400°, and atmospheric pressure (with the exception of TiI_4).

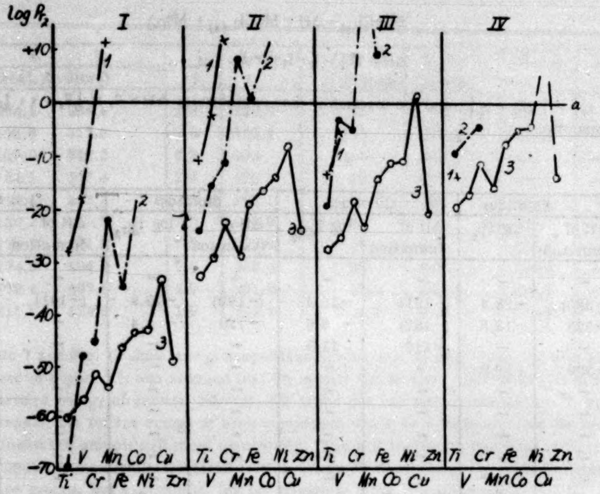

Fig. 9. Variation of the logarithm of the dissociation pressure of halides at 400° in the transition from Ti to Zn.

I) Fluorides, II) chlorides, III) bromides, IV) iodides.

1) $2MeX_4 \rightleftharpoons 2MeX_3 + X_2$, 2) $2MeX_3 \rightleftharpoons 2MeX_2 + X_2$; 3) $MeX_2 \rightleftharpoons Me + X_2$.

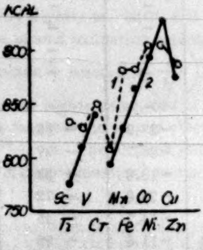

Fig. 10. Enthalpy of disproportionation of MeCl compounds as the distance between the curves $E_2 + s + I_1$ (1) and $2E_1 + I_2$ (2).

On the question of the possible existence of compounds of univalent metals of the first sub-period, it may be concluded that compounds of a given valency cease to exist either because the dissociation pressure of the compound at the given temperature is very high, or because the compound is capable of disproportionation. The first is probable for compounds of the highest valency of a particular element. On the other hand, compounds of the lower valencies may disappear owing to the disproportionation reaction, and if both products of this reaction are formed in the solid state, then the reaction will only proceed readily if it is exothermic. In that case the following reaction is possible:

$$2MeCl_{(s)} = MeCl_{2(s)} + Me_{(s)}.$$

This process may be broken down into the following stages: the crystal lattice of MeCl must be destroyed (E_1), energy to detach an electron from a single ion of the metal Me^+ must be expended (I_2), energy from the transfer of this electron to another ion of the metal is evolved (I_1), energy of sublimation of the metal formed (s) and lattice energy of the salt $MeCl_2$ formed (E_2) is evolved.

$$2MeCl_{(s)} + 2E_1 = 2Me^+ + 2Cl^-$$

$$Me^+ + I_2 = Me^{++} + e^-$$

$$Me^+ + e^- - I_1 = Me_{(gas)}$$

$$Me_{(gas)} - s = Me_{(s)}$$

$$Me^{++} + 2Cl^{-} - E_2 = MeCl_{2(s)}$$

$$2MeCl_{(s)} + \Delta H = MeCl_{2\,(s)} + Me_{(s)}$$

$$\Delta H = 2E_1 + I_2 - I_1 - s - E_2.$$

$\Delta H < 0$, if $|E_2 + s + I_1| > |2E_1 + I_2|$, and the reaction is then exothermic; $\Delta H > 0$, if $|E_2 + s + I_1| < |2E_1 + I_2|$ – the reaction is endothermic.

TABLE 6

Dissociation of halides		Fluorides		Chlorides		Bromides		Iodides	
		ΔH of formation	log P_{F_2}	ΔH of formation	log P_{Cl_2}	ΔH of formation	log P_{Br_2}	ΔH of formation	log P_{I_2}
$2MeX_4 = 2MeX_3 + X_2$	Sc	–	–	–	–	–	–	–	–
	Ti	(–380)	–28.4	(–191)	–10.9	(–180)	–13.9	(–141)	–14.0
	V	–325	–18.5	(–162)	– 2.6	–129	– 5.4	–	–
	Cr	–	–	–110	+11.9	–	–	–	–
	Mn	–230	+10.9	–	–	–	–	–	–
	Fe	–	–	–	–	–	–	–	–
	Co	–	–	–	–	–	–	–	–
	Ni	–	–	–	–	–	–	–	–
	Cu	–	–	–	–	–	–	–	–
	Zn	–	–	–	–	–	–	–	–
$2MeX_3 = 2MeX_2 + X_2$	Sc	–367	–	–221	–	–190.4	–	–149	–
	Ti	(–325)	–69.4	(–175)	–24.9	–143	–19.6	–102	– 9.6
	V	–285	–48.3	(–160)	–19.0	–120	– 3.4	–	–
	Cr	–266	–45.6	–143	–14.5	–102•	– 5.1	– 99.2	– 4.3
	Mn	–238	–22.6	–110	+ 8.3	–	–	–	–
	Fe	–23.5	–35.0	– 96	+ 0.3	– 76	+ 4.0	–	–
	Co	–	–	–	–	–	–	–	–
	Ni	–	–	–	–	–	–	–	–
	Cu	–	–	–	–	–	–	–	–
	Zn	–	–	–	–	–	–	–	–
$MeX_2 = Me + X_2$	Sc	–	–	–	–	–	–	–	–
	Ti	(–210)	–59.8	–125	–32.7	–110	–27.9	– 85	–19.5
	V	–185	–52.1	–117	–29.9	–104	–25.7	– 77	–17.2
	Cr	–182	–51.5	–103	–22.9	– 81	–18.8	– 58	–11.5
	Mn	–190	–54.0	–111.6	–29.0	– 96	–23.6	– 72	–15.7
	Fe	–168	–46.6	– 82	–19.3	– 69	–14.7	– 45	– 7.6
	Co	–158	–43.7	– 72	–16.7	– 56.4	–11.6	– 36	– 4.9
	Ni	–158	–43.4	– 70.6	–14.6	– 55.8	–11.2	– 38	– 4.6
	Cu	–128	–33.6	– 46	– 8.5	– 34.0	+ 1.5	–	–
	Zn	–176	–49.1	– 99.6	–24.6	– 85.7	–20.5	– 64.7	–14.1

• The dissociation pressures of fluorides, bromides, and iodides were calculated from [1], and the dissociation pressures of $CrBr_3$ [17] and of CrI_3 [18] were determined by ourselves.

If it is assumed that the symbatic relationship between the lattice energy and the ionization potential is applicable also to compounds of univalent metals of the first sub-period, then, as Fig. 2 shows, the first ionization potential gradually increases in the transition from Sc to Zn, but the increase is very slow, and I_1 is practically constant from Sc to Cr (Table 7),   from Mn to Cu, and   is a little greater for Zn. In this case the crystal lattice energy, which should increase even more slowly than the ionization potential, will have an almost constant value. Consequently, the MeCl lattice energy for all these elements, with the exception of zinc, should be either less than, or equal to, the lattice energy of CuCl. Let us assume that the MeCl lattice energy is equal to the CuCl lattice energy (231 kcal./mole) and let us calculate the change of enthalpy in the disproportionation reaction. The values of ΔH obtained are shown in Table 7.

TABLE 7

Element	I_1	I_2	$\frac{I_2}{I_1}$	I_2-I_1	s (kcal./ / g-atom)	E_2 (kcal./ /mole)	$2E_1+I_2$	E_2+s+I_1	ΔH (kcal.)
	(kcal./g-atom)								
Sc	154.1	294.4	1.9	140.3	70	–	–	–	–
Ti	156.6	312.8	2.0	156.2	100	577.4	774.8	−834.0	−59.2
V	155.0	348.0	2.2	193	85	588	810	−828	−18
Cr	154.1	377.4	2.4	223.3	89.4	607	839.4	−850.5	−11.1
Mn	170.4	333.5	1.9	163.1	69.7	568	795.5	−808.1	−12.6
Fe	180.1	365.7	2.0	185.6	96.7	607.5	827.7	−884.3	−56.6
Co	179.4	401.8	2.2	122.4	85	621	863.8	−885.4	−21.6
Ni	174.8	434.2	2.5	259.4	85	647.6	896.2	−907.4	−11.2
Cu	176.4	467.6	2.7	291.2	81.2	649.4	929.6	−907.6	+22.6
Zn	215.5	414.9	1.9	199.4	31.2	643.9	876.9	−890.6	−13.7

As Table 7 and Fig. 10 show, the disproportionation reaction of MeCl proceeds with absorption of energy only in the case of copper. It was assumed that the crystal lattice energy of compounds of the type MeCl is always equal to the lattice energy of cuprous chloride, but as the first ionization potential of Ti, V, Cr, Mn, and Ni is less than that of copper, the lattice energy of their compounds should be a little less than the lattice energy of CuCl, which would make the process still more exothermic. The first ionization potential of Fe, Co, and Ni is greater than that of copper; consequently the MeCl lattice energy for these elements should be somewhat greater, which would make the process less exothermic, but not enough to make it endothermic.

How is this special position of copper in comparison with the other elements to be explained? The disproportionation reaction is exothermic if: $|E_2 + s + I_1| > |2E_1 + I_2|$, that is, when the lattice energy of the dihalide formed, the sublimation energy of the metal, and the first ionization potential exceed the expenditure of energy in the destruction of the monohalide lattice and removal of the second electron from the metal ion.

From Table 7 it is seen that the lattice energy of $CuCl_2$ is higher than the lattice energies of the other dihalides, but only slightly so. $NiCl_2$ and $ZnCl_2$ have almost the same lattice energies as $CuCl_2$. The maximum in the case of the second ionization potential, however, is much more prominent. If we take the ratio of the first and second ionization potentials $\left(\frac{I_2}{I_1}\right)$, we see that while for most of the elements this ratio is close to two, copper has a much higher value, nearer to three (2.7). This high value of the second ionization potential is explained by the fact that the second electron lost by the copper is not an s-electron, but a d-electron from the completed $3d^{10}$-layer. The difficulty of removal of the second electron favors the fact that the expenditure of energy in the disproportionation reaction is not compensated by the evolution of energy in the formation of $CuCl_2$ and Cu.

Disproportionation of MeCl compounds is also often favored by evolution of a large amount of energy during formation of the metal, that is, by a high sublimation energy. This is not so in the case of copper, the sublimation energy of copper is relatively low. The influence of sublimation energy is more pronounced for the elements of the second and third sub-periods.

SUMMARY

1. It is shown, by a comparison of the dissociation pressures of the elements in the first sub-period, that these pressures change symbatically with the second ionization potential in the transition from one element to another.

2. It is shown that the crystal lattice energies of a number of compounds, both of the elements of the main sub-groups and of the elements of the sub-periods, vary symbatically with changes of the ionization potentials of the metals.

3. It is shown that the dissociation pressures of the tri- and tetrachlorides of the elements of the first sub-period are symbatic with the third or fourth ionization potential respectively of the metal component. On the basis

of this relationship it is possible to predict the possibility or impossibility of synthesizing certain hitherto unknown compounds of a given degree of oxidation of a particular element.

4. On the basis of the symbatic course of the lattice energies and the ionization potentials it is shown why copper forms compounds in which it is univalent. The explanation lies in the high value of the second ionization potential of copper atoms and the relatively low sublimation energy of this metal.

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INTERACTION OF NITRATES AND NITRITES OF THE METALS OF THE FIRST AND SECOND GROUPS OF D. I. MENDELEEV'S PERIODIC SYSTEM IN MELTS

XIII. ELECTRICAL CONDUCTIVITY OF THE BINARY SYSTEMS CESIUM NITRATE – CADMIUM NITRATE, THALLIUM NITRATE – CADMIUM NITRATE, AND POTASSIUM NITRATE – RUBIDIUM NITRATE

P. I. Protsenko and N. P. Popovskaya

Systematic measurements of the electrical conductivities of binary systems in the molten state containing cadmium nitrate as one component and lithium, sodium, potassium, rubidium, cesium, thallium, or silver nitrate as the other, showed that in all these cases the numerical values of the conductivity steadily increase from components of lower to components of higher conductivity; it is noteworthy that the isothermal conductivity curves do not have any distinguishing points which indicate chemical action between the components even when the fusion curves of the diagrams of state for the binary systems, obtained by the visual polythermic method of physicochemical analysis, clearly show the existence of chemical compounds: $Cd(NO_3)\cdot 2KNO_3$, $Cd(NO_3)_2\cdot 2RbNO_3$, $Cd(NO_3)_2\cdot 2AgNO_3$, $LiNO_3\cdot RbNO_3$, $AgNO_3\cdot RbNO_3$, $AgNO_3\cdot 2RbNO_3$ [1-5].

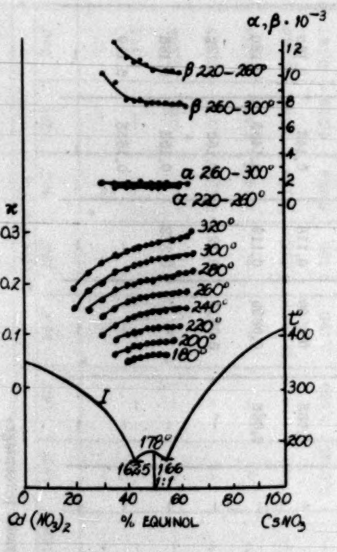

Fig. 1. The system $Cd(NO_3)_2-CsNO_3$. κ) conductivity $\alpha\cdot 10^{-3}$ and $\beta\cdot 10^{-3}$ are the absolute and relative temperature coefficients. I) The fusion curve for the system.

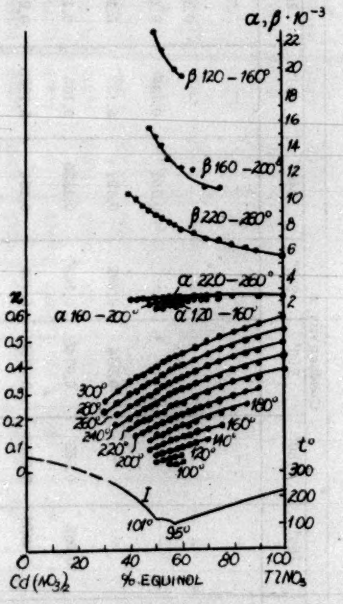

Fig. 2. The system $Cd(NO_3)_2-TlNO_3$. κ) conductivity; $\alpha\cdot 10^{-3}$ and $\beta\cdot 10^{-3}$ are the absolute and relative temperature coefficients. I) The fusion curve for the system.

TABLE 1

	Conductivity, κ									Absolute and relative temperature coefficients			
										220-260°		260-300°	
$CsNO_3$•	160°	180°	200°	220°	240°	260°	280°	300°	320°	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
20	–	–	–	–	–	–	–	0.153	0.190	–	–	–	–
25	–	–	–	–	–	–	0.148	0.1835	0.221	–	–	–	–
30	–	–	–	–	0.103	0.136	0.1695	0.2045	0.240	–	–	1.712	10.07
35	–	–	0.064	0.092	0.121	0.153	0.187	0.2235	0.258	1.525	12.50	1.762	9.38
40	0.032	0.052	0.0745	0.104	0.1335	0.165	0.1975	0.2300	0.2625	1.525	11.38	1.625	8.22
42.5	0.0355	0.0565	0.0795	0.108	0.136	0.1685	0.201	0.234	0.268	1.513	11.00	1.638	8.14
45	–	0.060	0.0830	0.110	0.141	0.1725	0.206	0.239	0.271	1.563	11.07	1.663	8.09
47.5	–	0.063	0.0860	0.115	0.145	0.1765	0.209	0.242	0.275	1.538	10.69	1.638	7.82
50	–	0.064	0.0890	0.117	0.146	0.178	0.210	0.245	0.279	1.525	10.37	1.675	7.93
52.5	–	0.065	0.0900	0.118	0.148	0.180	0.212	0.247	0.281	1.550	10.42	1.675	7.86
55	–	0.066	0.0895	0.119	0.1485	0.180	0.213	0.249	–	1.5375	10.29	1.713	7.94
57.5	–	–	0.0910	0.120	0.150	0.182	0.215	0.250	0.283	1.550	10.29	1.675	7.76
60	–	–	–	0.123	0.153	0.186	0.220	0.255	0.288	1.575	10.23	1.725	7.82
62.5	–	–	–	–	0.1555	0.189	0.222	0.257	0.2905	–	–	1.700	7.63
65	–	–	–	–	–	–	0.226	0.262	0.300	–	–	–	–

• In equimolar percentages

TABLE 2

	Conductivity, κ											Absolute and relative temperature coefficients					
$TlNO_3$*	100°	120°	140°	160°	180°	200°	220°	240°	260°	280°	300°	120-160°		160-200°		220-260°	
												$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
30	–	–	–	–	–	–	–	–	–	0.220	0.261	–	–	–	–	–	–
35	–	–	–	–	–	–	–	0.171	0.215	0.2595	0.304	–	–	–	–	–	–
40	–	–	–	–	–	–	0.164	0.205	0.249	0.295	0.340	–	–	–	–	2.13	10.30
42.5	–	–	–	–	–	0.136	0.177	0.220	0.264	0.309	0.354	–	–	–	–	2.18	9.90
45	–	–	–	–	–	0.1485	0.190	0.234	0.278	0.323	0.369	–	–	–	–	2.20	9.40
47.5	–	–	–	0.0825	0.1165	0.156	0.199	0.244	0.288	0.334	0.380	–	–	1.825	15.4	2.23	9.20
50	–	0.0345	0.060	0.092	0.130	0.170	0.213	0.257	0.303	0.349	0.396	1.42	22.7	1.95	14.8	2.25	8.70
52.7	–	0.042	0.0715	0.104	0.142	0.184	0.228	0.275	0.322	0.369	0.415	1.55	21.3	2.00	14.0	2.35	8.52
55	0.026	0.049	0.080	0.1185	0.156	0.200	0.247	0.294	0.341	0.387	0.434	1.75	21.2	2.02	12.9	2.35	8.00
57.5	0.0295	0.054	0.086	0.124	0.165	0.210	0.258	0.306	0.353	0.401	0.448	1.75	19.9	2.15	12.9	2.38	7.80
60	0.033	0.059	0.093	0.1325	0.174	0.219	0.266	0.315	0.369	0.410	0.457	1.85	19.5	2.15	12.3	2.38	7.60
62.5	–	–	0.100	0.136	0.177	0.229	–	0.320	0.375	–	–	–	–	–	–	–	–
65	–	–	0.106	0.144	0.188	0.235	0.283	0.330	0.380	0.427	0.474	–	–	2.28	12.28	2.43	7.35
70	–	–	0.122	0.161	0.206	0.254	0.303	0.351	0.400	0.448	0.495	–	–	2.25	10.9	2.43	6.90
75	–	–	–	0.172	0.220	0.268	0.318	0.368	0.417	0.467	0.517	–	–	2.40	10.9	2.48	6.80
80	–	–	–	–	0.239	0.289	0.339	0.389	0.4385	0.488	0.537	–	–	–	–	2.50	6.50
85	–	–	–	–	0.250	0.302	0.352	0.402	0.451	0.501	0.551	–	–	–	–	2.48	6.15
90	–	–	–	–	–	0.317	0.367	0.4165	0.467	0.516	0.566	–	–	–	–	2.50	6.05
100	–	–	–	–	–	–	0.396	0.446	0.498	0.548	0.599	–	–	–	–	2.55	5.72

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* In equimolar percentages.

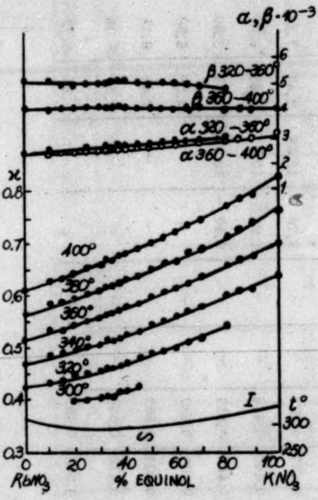

Fig. 3. The system $RbNO_3-KNO_3$. κ) conductivity; $\alpha \cdot 10^{-3}$ and $\beta \cdot 10^{-3}$ are the absolute and relative temperature coefficients. I) The fusion curve for the system; ∾ continuous solid solutions.

To confirm the formation of the additionally established compounds $Cd(NO_3)_2 \cdot 2CsNO_3$ and $Cd(NO_3)_2 \cdot 2TlNO_3$ in melts at the moment when the first crystals appear, and to study more deeply the possibility of applying conductivity measurements on melts as a method of physicochemical analysis, although this problem has been solved by a number of workers [6-9], we have examined, in addition to the binary systems described previously [10, 11] three more systems: $Cd(NO_3)_2-CsNO_3$, $Cd(NO_3)_2-TlNO_3$ and $RbNO_3-KNO_3$, which are discussed (Figs. 1, 2 and 3).

Study of the binary system $Cd(NO_3)_2-CsNO_3$ showed that chemical action takes place between the nitrates of cadmium and cesium, to form the compound $Cd(NO_3)_2 \cdot 2CsNO_3$ with melting point 178° (Fig. 1).

In the binary system $Cd(NO_3)_2-TlNO_3$ the nitrates of cadmium and thallium also react chemically and form the complex compound $Cd(NO_3)_2 \cdot 2TlNO_3$ which melts with decomposition (Fig. 2).

In the binary system $RbNO_3-KNO_3$ the components form a continuous series of solid solutions with a weakly defined minimum on the fusion curve (Fig. 3).

EXPERIMENTAL

The conductivity measurements were carried out with apparatus set up essentially according to Kohlrausch's scheme, with a number of important modifications and improvements described by Barzakovsky [12] and by Belyaev and Mironov [8, 9].

The source of high frequency current was a tube generator which provided a regular supply of sinusoidal electric vibrations. The construction of the generator was such that the frequency range could be varied between 1200 and 2400 cycles per second, with intermediate stages of 1500 and 1900 cycles. The electrical conductivity measurements were carried out at a frequency of 1200 cycles with an output voltage of 6 V.

The platinum electrodes were mounted in a cell of heat-resisting glass, similar in shape to the cell used by Biltz [13] for the measurement of the electrical conductivity of fused salts. The cell was calibrated with the aid of twice-recrystallized chemically pure fused potassium nitrate. The numerical values of the conductivity of potassium nitrate at different temperatures, needed to calculate the cell capacity, were taken from the paper by Jeger and Kapma [14].

The cell constant was systematically checked during the experiments. The electrical conductivity was measured polythermally at 5-8° intervals, in the 100-400° temperature range.

The numerical values of the electrical conductivity, and also of the absolute and relative temperature coefficients, were calculated with the use of a formula, as before [11].

Isotherms, at 20° intervals, were plotted for all the three systems from the data of the polytherms obtained, (Figs. 1, 2, 3). The content of the components in the mixture for the various systems is expressed in equimolar percentages.

DISCUSSION OF RESULTS

As is seen from Figs. 1 and 2 and the data of Tables 1 and 2, the isothermal conductivity curves for the systems $Cd(NO_3)_2-CsNO_3$ and $Cd(NO_3)_2-TlNO_3$ do not have any distinctive points. They all rise steadily from the least conducting cadmium nitrate to the more conducting nitrates of cesium and thallium. It is interesting to note that the isotherms deviate somewhat from additivity in the direction of higher conductivity values.

The isothermal conductivity curves for the system

$RbNO_3-KNO_3$

also steadily rise from the less conducting rubidium nitrate to the more conducting potassium nitrate. In contrast to the isothermal curves for the first two systems, they show a small deviation from additivity in the direction of lower conductivity values (Fig. 3, Table 3).

TABLE 3

	Conductivity, κ						Absolute and relative temperature coefficients			
KNO_3 *	300°	320°	340°	360°	380°	400°	320-360°		360-400°	
							$a \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$a \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
0	–	0.422	0.470	0.516	0.563	0.608	2.35	5.19	2.3	4.08
10	–	0.435	0.485	0.535	0.581	0.629	2.5	5.15	2.35	4.03
15	–	0.438	0.486	0.534	0.582	0.630	2.4	4.93	2.4	4.11
20	0.397	0.446	0.494	0.544	0.593	0.642	2.45	4.95	2.45	4.13
25	0.400	0.449	0.500	0.550	0.601	0.650	2.525	5.05	2.5	4.14
30	0.402	0.454	0.504	0.555	0.606	0.656	2.525	5.06	2.525	4.16
32.5	0.406	0.459	0.512	0.564	0.614	0.666	2.625	5.11	2.55	4.12
35	0.408	0.460	0.511	0.564	0.615	0.666	2.6	5.08	2.55	4.125
37.5	0.413	0.464	0.517	0.570	0.622	0.674	2.65	5.125	2.6	4.14
40	0.417	0.470	0.522	0.576	0.628	0.679	2.65	5.08	2.58	4.102
45	0.423	0.476	0.529	0.582	0.635	0.686	2.65	5.00	2.6	4.1
50	–	0.488	0.541	0.596	0.647	0.699	2.7	4.98	2.575	4.01
55	0.438	0.492	0.548	0.602	0.656	0.708	2.75	5.03	2.65	4.02
60	0.444	0.499	0.556	0.610	0.664	0.718	2.775	5.00	2.7	4.05
65	–	0.509	0.566	0.621	0.676	0.732	2.8	4.95	2.78	4.07
70	–	0.519	0.575	0.632	0.687	0.743	2.825	4.91	2.775	4.02
80	–	0.542	0.598	0.656	0.712	0.769	2.85	4.76	2.825	3.95
85	–	–	0.604	0.664	0.722	0.780	–	–	2.9	4.0
90	–	–	0.610	0.670	0.729	0.787	–	–	2.925	4.0
100	–	–	0.635	0.6975	0.7598	0.821	–	–	3.075	4.05

The curves for the absolute temperature coefficient *a*, calculated from the conductivity data for the temperature ranges 220-260, 260-300° (Fig. 1, Table 1); 120-160, 160-200° (Fig. 2, Table 2); 320-360, 360-400° (Fig. 3, Table 3) are all almost linear. The curves for the relative temperature coefficient β, calculated for the same temperature ranges as the values of the absolute temperature coefficient *a*, also do not have any distinctive points (Figs. 1-3, Tables 1-3).

The eight systems studied, including those previously described, the components of which interact chemically, do not show any distinctive points on the isothermal conductivity curves which indicate chemical action between the components. Nevertheless it must be stressed again that chemical compounds, clearly shown by the fusion curves, have been established for all these systems by the visual polythermic method of physicochemical analysis.

It follows from the above that there is no correlation in the systems examined between the fusion curves and the isothermal conductivity curves.

Similar cases have been described previously [16, 17]. However, in their generally correct discussions of the problem, the authors concerned relied on insufficient experimental data, and therefore their opinion was not confirmed.

On the other hand, the researches of Bergman and Chagin [6], Luzhanaya and Vereshchetina [15], Tarasova [7], and Belyaev and Mironov [8, 9] showed that when chemical compounds, established by the visual polythermic method of physicochemical analysis, are formed in melts, minima are observed on the isothermal conductivity curves. On the basis of these results, some of the above authors tended to regard as inaccurate the measurements of workers who did not succeed in showing minima on the isothermal conductivity curves corresponding to chemical compounds, while electrical conductivity, as a method of physicochemical analysis, was regarded as a very sensitive method [6-9]. In our opinion, more often there will be no correlation between the fusion and the conductivity curves, for the following reasons.

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* In equimolar percentages.

Fusion curves obtained by the visual polythermic method of physicochemical analysis, reflect the actual nature of the interaction between the components at the solid-liquid interphase at the instant when the first crystals appear, that is, along the liquidus curve. In these conditions the state of the components and the chemical compounds formed is characterized by ideally regular structure of their structural components — crystals, with strict orientation of ions. The isothermal electrical conductivity curves, on the other hand, reflect the state of the components in the fused salt medium, that is, in the liquid phase, and often at temperatures well above the liquidus curve. In these conditions the strictly oriented ionic order characteristic of solid crystals is so changed that the crystals cease to exist as such and pass into an amorphous liquid state, which constitutes, in the present instance, a mixture of "free" positive and negative ions, with a high conductivity.

The abrupt jump from the solid crystalline state into the liquid (fused) state, in our opinion, is accompanied by complete autodissociation * into "free" ions, which happens in the chemical compounds established by us: $Cd(NO_3)_2 \cdot 2KNO_3$, $Cd(NO_3)_2 \cdot 2CsNO_3$, $Cd(NO_3)_2 \cdot 2AgNO_3$, $Cd(NO_3)_2 \cdot 2TlNO_3$, and also in the chemical compounds described by Pushin [1] and Palkin [2], $LiNO_3 \cdot RbNO_3$, $AgNO_3 \cdot 2RbNO_3$ the electrical conductivity of which was studied by us.

It must be assumed that during the first instant of autodissociation the complex molecules break up into the individual components. The molecules of the components formed (the substances taken originally) in turn undergo autodissociation into "free" ions. The autodissociation of the molecules into free ions of one of the above double salt complexes in melts may be represented by the following scheme:

$$Cd(NO_3)_2 \cdot 2KNO_3 \longrightarrow Cd(NO_3)_2 + 2KNO_3 \rightleftharpoons Cd^{\cdot\cdot} + 2K^{\cdot} + 4NO_3^{'}.$$

From the high conductivity of nitrates in melts it may be assumed that their degree of autodissociation will be near to or equal to 100%. In all instances such as those described above, the isothermal electrical conductivity curves will not have any minima to correspond to chemical compounds established by the visual polythermic method of physicochemical analysis.

On the basis of the above considerations it may be assumed that in all analogous cases there will not be any correlation between the fusion curves and the conductivity curves. We may therefore conclude that if the use of electrical conductivity as a method of physicochemical analysis is applicable to melts at all, this is far from always true, and with considerable reservations.

SUMMARY

1. The electrical conductivity of nitrate mixtures in melts of three binary systems: $Cd(NO_3)_2-CsNO_3$, $Cd(NO_3)_2-TlNO_3$ and KNO_3-RbNO_3 has been measured and the data used to calculate the absolute and relative temperature coefficients.

2. It is shown that the isothermal conductivity curves steadily rise from the less conducting nitrates of cadmium and rubidium to the more conducting nitrates of thallium, potassium, and cesium, and they do not have any distinctive points, and therefore show no correlation with the liquidus curves obtained by the visual polythermic method of physicochemical analysis.

3. A mechanism is proposed for the autodissociation of double-salt type complexes in melts, formed from nitrates of the first and second groups of Mendeleev's periodic system.

4. It is established that electrical conductivity is not applicable as the basis for a method of physicochemical analysis of melts containing nitrate components, as the conductivity isotherms are always obtained of approximately the same form irrespective of the type of liquidus diagram.

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PHYSICOCHEMICAL STUDY OF AQUEOUS-DIOXANE SOLUTIONS

VII. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN AQUEOUS DIOXANE •

Ya. F. Mezhenny

Some physicochemical properties of hydrogen chloride solutions in dioxane were described previously [1]. The present study consisted of an investigation of the electrical conductivity of hydrogen chloride in dioxane-water mixtures with different dielectric constants. The values of the dielectric constants of a number of such mixtures of the same composition as those used by Kraus and Fuoss [2] were taken from that paper. Values for mixtures not given by Kraus and Fuoss were determined graphically. The hydrogen chloride solutions in these solvents were prepared as described previously [1]. The concentrations of the solutions obtained were determined by the usual titration with caustic soda solution in presence of phenolphpthalein. Systems with very high dioxane content, and also in anhydrous dioxane, were diluted with water before titration. The solutions of hydrogen chloride in dioxane-water solvent were used in the following dilutions: 10, 100, and 1000 liters/g-equiv. This choice of dilutions made it possible to plot the equivalent conductivity – dilution curves in the region which approached a horizontal line, which was the region of greatest interest in this study. The electrical conductivity of each system was studied at 20, 30, and 40°.

The results of Table 1 show that as the dioxane content of the medium increases and the dielectric constant DC decreases, λ of the HCl solutions decreases, and when the dielectric constant of the medium falls to 8 (10 times as small as DC for water), the equivalent conductivity of the hydrogen chloride solutions is only a few units (that is, its value decreases nearly 100 times). In this medium, the dielectric constant of which is 8, 0.1 N hydrogen chloride solution has lower equivalent conductivity than 0.1 N acetic acid in water. The conductivity of 0.01 N acetic acid in water is, however, about 5 times the conductivity of hydrogen chloride in aqueous dioxane, which has DC equal to 8. If we take hydrogen chloride solutions in anhydrous dioxane, when DC = 2.21, then, as was shown previously [1], the electrical conductivity of such a solution at dilutions of 1000-10 liters/g-equiv. is negligible. Only at dilutions of the order of 0.2 does the equivalent conductivity reach values of the order of tenths of a unit, and the value falls with dilution according to the so-called "anomalous" curve $\lambda = f(v)$. Thus, here also, as for the various solvents studied by Kablukov, the electrical conductivity of hydrogen chloride solutions entirely depends on the dielectric constant of the aqueous dioxane medium. It is also interesting to note that similar values for the electrical conductivities of hydrogen chloride solutions are obtained irrespective of whether the solvent is pure or a mixture. Kablukov found, for solutions in methyl alcohol, the dielectric constant of which is 35.4, an equivalent conductivity of 117 at a dilution of 91.16; for a dioxane-water mixture (DC = 37) at the same dilution we have an equivalent conductivity of about 123.

The variation of the electrical conductivity of HCl solutions in dioxane-water mixtures on temperature (in the temperature range studied) is approximately represented by a linear function with different slopes to the temperature axis: it is greatest for systems with DC = 37; in systems with DC = 12, the temperature coefficient remains positive but has a lower absolute value.

λ_0 of hydrogen chloride solutions

As Table 1 shows, the $\lambda = f(v)$ curves for dioxane-water solutions of hydrogen chloride lie lower with decreasing DC of the medium (Fig. 1).

As is known, by transformation of the function $\lambda = f(v)$ into the function $\lambda = f(\sqrt{c})$ values of λ_0 may be obtained by extrapolation, that is, values of equivalent conductivity corresponding to $\alpha = 1$ (the classical theory).

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But, as Fig. 2 shows, the $\lambda = f(\sqrt{c})$ curves also lie lower with decreasing DC of the medium, and so the values of λ_0 decrease also, and when DC $\longrightarrow$ 1, $\lambda_0 \longrightarrow$ 0.

TABLE 1

Electrical Conductivity of Hydrogen Chloride in Aqueous Dioxane Media

Percentage of water in the dioxane mixture	DC	Dilution, liters/g-equiv.	Temperature	$\chi \cdot 10^3$	λ
82	60	10	20°	16.3	163
	60	100	20	2.02	202
	60	1000	20	0.215	215
53	37	10	20	8.76	87.6
	37	10	30	8.95	89.5
		10	40	12.0	120.0
	37	100	20	1.275	127.5
		100	30	1.523	152.3
		100	40	1.752	175.2
	37	1000	20	0.132	132.0
		1000	30	0.163	163.2
		1000	40	0.204	204.0
20.2	12	10	20	0.867	8.67
		10	30	1.05	10.5
	12	100	20	0.0936	9.36
		100	30	0.1027	10.27
		100	40	0.1062	10.62
	12	1000	20	0.011	11.0
		1000	30	0.021	21
		1000	40	0.025	25
14	8	10	20	0.261	2.61
		10	25	0.288	2.88
		10	30	0.303	3.03
		10	40	0.316	3.16
	8	100	20	0.0376	3.76
		100	25	0.0432	4.32
		100	30	0.0473	4.73
		100	40	0.0521	5.21
	8	1000	18	0.00405	4.05
		1000	20	0.00427	4.27
		1000	25	0.00452	4.52

It is known from the work of Owen and Waters [4], who measured the electrical conductivity of hydrogen chloride solutions in dioxane-water mixtures at DC = 60, 79, 38, 48, 27 and 9.53 at 25° (these results are also quoted in the book by Harned and Owen [5], p. 326) • that the equivalent conductivity curves plotted against the square root of the concentration also form a group of curves which lie lower with decreasing DC of the medium. This tendency of $\lambda_0 \longrightarrow$ 0 as DC of the medium tends to unity, follows both from Kablukov's data [3] and from the data of other workers (Table 2).

These results can be explained only if we admit the possibility of the process $H^{\cdot} + Cl^{\cdot} \longrightarrow HCl$ which goes increasingly toward the right as the dielectric constant of the medium decreases, even in very dilute solutions.

• Although Chapter 11 of this book is exclusively devoted to the properties of HCl solutions, it makes no mention whatever of the classic investigations by the Russian scientist I. A. Kablukov, who was the first to study the electrical conductivity of non-aqueous solutions of hydrogen chloride.

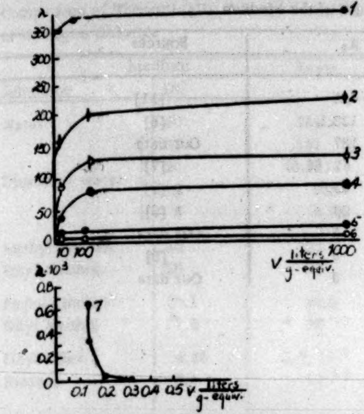

Fig. 1. Variation of the equivalent conductivity of HCl solutions in dioxane-water medium at 20°.
1) In water (DC = 80), 2) in dioxane-water medium (DC = 60), 3) in dioxane-water medium (DC = 37), 4) the same for DC = 20, 5, 6) the same, with increase of dioxane content and decrease of DC to 12 and 8 respectively, 7) the same for pure dioxane, with DC = 2.1.

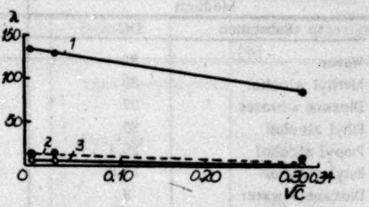

Fig. 2. $\lambda = f(\sqrt{c})$ for dioxane-water solutions of hydrogen chloride.
1) At DC = 37, 2) at DC = 12, 3) at DC = 8.

The values for λ_0 determined by ourselves from Fig. 2 for media with low dielectric constants, like the values obtained by Owen and Harned [5], are meaningless, as these values for the equivalent conductivity do not correspond to that state of the electrolyte ($\alpha = 1$) which is necessary for λ_0 and which the theory of strong electrolytes demands for all media. Semenchenko [6] was right in pointing out "that in solvents with low dielectric constants molecularization of ions, and even formation of complex ions and molecules is possible, which is completely ignored by the Debye-Onsager theory" (italics ours). This is also indicated by the $\lambda = f\,\frac{1}{D}$ curve for solutions of HCl in any medium (Fig. 3).

If the data obtained in the present study are used to plot the graph for the function

$$\log \frac{\lambda_u}{\lambda_p} = f\,\frac{1}{D}\,. \tag{1}$$

then this will be a straight line which does not pass through the origin; therefore, for hydrogen chloride solutions, the equation for the relationship between λ and D may be given in the form

$$\lambda_p = \lambda_u \cdot 10^{-\left(20.5 \cdot \frac{1}{D} + 0.5\right)} \tag{2}$$

or

$$\lambda_p = 1500 \cdot 10^{-\left(20.5 \cdot \frac{1}{D} + 0.5\right)}$$

Quite obviously this equation loses its meaning when $\frac{1}{D} \approx 0$, since when $D \longrightarrow \infty$ and $\frac{1}{D} \longrightarrow 0$, not only ionic triads but simple undissociated molecules are absent, as is the mobility-decreasing action of the charge of one ion on another; therefore in such conditions the equations (2) become

$$\log \frac{\lambda_u}{\lambda_p} = k \cdot \frac{1}{D} \tag{3}$$

or

$$\lambda_p = \lambda_u \cdot e^{-k \cdot \frac{1}{D}}\,. \tag{4}$$

TABLE 2

Decrease of the Values of λ_0 of HCl Solutions with Decrease of DC of the Medium

Medium		t°	λ_0	Sources
Substance	DC			
Water	80	25	≈ 425	[11]
Methyl alcohol	33	25	133.1	[6]
Dioxane + water	37	18	137	Our data
Ethyl alcohol	25	25	62 (66.5)	[7]
Propyl alcohol	20.1	25	46.6	[9]
Butyl alcohol	17.8	25	20	[9]
Dioxane + water	8	20	≈ 5	Our data
Benzene	2.2	18	≈ 0	[3]
Dioxane	2.1	18	≈ 0	Our data

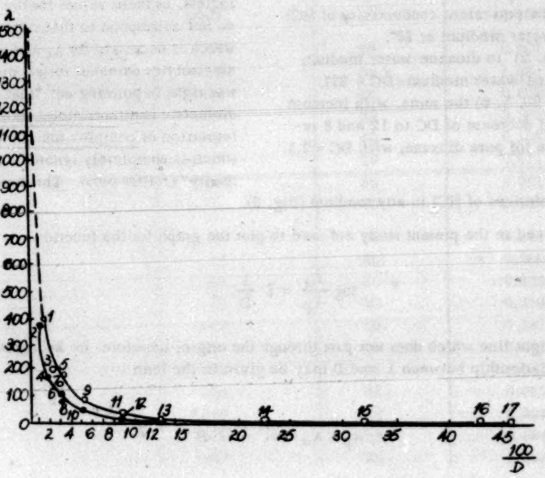

Fig. 3. $\lambda = f\left(\frac{1}{D}\right)$ for hydrogen chloride solutions.

1) Aqueous solution, v = 1000 liters/g-equiv., 2) aqueous solution, v = 10 liters/g-equiv., 3) dioxane-water solution for DC = 60 and v = 1000 liters/g-equiv., 4) dioxane-water solutions for DC = 60 and v = 10 liters/g-equiv., 5) in methyl alcohol for DC = 33 and v = 1000 liters/g-equiv. [9], 6) in methyl alcohol for DC = 33 and v = 10 liters/g-equiv., 7) dioxane-water solution for DC = 37 and v = 1000 l/g-equiv., 8) dioxane-water solution for DC = 37 and v = 10 liters/g-equiv., 9) dioxane-water solution for DC = 20 and v = 1000 liters/g-equiv., 10) dioxane-water solution for DC = 20 and v = 10 liters/g-equiv., 11, 12) dioxane-water solutions for DC = 12 and v = 1000 and 10 liters/g-equiv., 13) dioxane-water solution for DC = 8 and v = 1000 liters/g-equiv., 14) in ethyl ether for DC = 4.5 [3], 15) dioxane- water solution for DC = 2.12 [10], 16) in benzene for DC = 2.28 [3], 17) in dioxane for DC = 2.1.

The results of a check of the agreement between data calculated from Equations 1-3 and experimental data obtained both by ourselves and by other workers in various media are shown in Table 3.

TABLE 3

Comparison of Theoretically Calculated and Experimentally Determined Values of the Equivalent Conductivity of Hydrogen Chloride

Medium		$\lambda_{calc.}$	$\lambda_{exp.}$	Source	Relative deviation (%)
Substance	DC				
Water	80	264	370	Tech. Encyclopedia	40
Dioxane + water	37	137	132	Our data	− 3
	20	44	58		30
	12	9.8	11		12
	8	4.52	4.05		−10
Methyl alcohol	33	113	133	[12]	17
Ethyl alcohol	25	72	74		2
Propyl alcohol	20.1	44.2	37.26	[13]	−20
Butyl alcohol	17.8	33	18.53		−44
Ethyl ether	4.45	$1.7 \cdot 10^{-2}$	$0.58 \cdot 10^{-2}$	[8]	−60
Dioxane	2.1	$10^{-6.5}$	Very small for v = 1000	Our data	Same order of magnitude

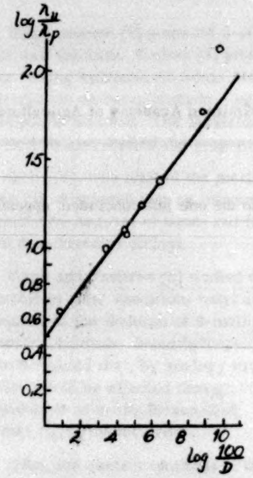

Fig. 4. Variation of $\log \frac{\lambda u}{\lambda p}$ with $\frac{1}{D}$ for hydrogen chloride solutions.

The data of Table 3 shows that the order of magnitude of the equivalent conductivity of hydrogen chloride solutions may be predicted with the aid of the mathematical relationships (1, 3).

In 11 instances when the theoretically calculated and experimentally found values of the electrical conductivity were compared, 2 showed a relative deviation from 3 to 2%; 4 gave relative deviations from −20 to 30%, 2 gave relative deviations from −40 to 40%, and only one gave a relative deviation of −60%; here, as was already pointed out for media with larger values of DC (80), the term B in equation (3) should increasingly lose its meaning, and therefore it is better to use equation (4) for such media.

The agreement, shown in Table 3, between the calculated and the experimental values of electrical conductivity confirms the validity of the view that the ions of a strong electrolyte form molecules when it is transferred to media with decreasing values of the dielectric constant, even in greatly diluted solutions.

As is known [6], the Kohlrausch-Onsager equation, even with such a conveniently investigated electrolyte as an aqueous solution of potassium chloride (which is nonvolatile, non-hygroscopic, stable to oxidation and reduction, etc.), gives results which deviate by 32.2 to 21.4% from the experimental results, and therefore the agreement of our experimental data with those calculated with the aid of equations (1, 2) should be regarded as satisfactory.

SUMMARY

1. The specific and equivalent conductivities of hydrogen chloride in aqueous dioxane solutions at DC between 80 and 2.1 have been measured.

2. It is shown that the equivalent conductivity of hydrogen chloride solutions decreases regularly with decreasing DC of the medium. The explanation for this is that when DC $\longrightarrow$ 1, $a \longrightarrow 0$ and $\lambda_0 \longrightarrow 0$.

3. The agreement between the values of the equivalent conductivity calculated with the aid of the proposed equation and the experimental values has been checked. Satisfactory agreement was found.

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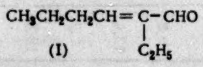
* In J. Gen. Chem. 1954 the only other article by this author in addition to the one just concluded, appears on page 1945, T.p. 1911. (T.p. = C. B. Translation pagination) – Publisher

STUDY OF THE CATALYTIC CONVERSION OF ALCOHOL INTO HYDROCARBONS OF THE DIVINYL SERIES

XVIII. CONTACT CONVERSION OF BUTYRALDEHYDE INTO 2-ETHYLHEXEN-2-AL

Yu. A. Gorin, K. N. Charskaya, and V. P. Litvinovskaya

In the presence of certain alkaline and also acid agents butyraldehyde undergoes aldol condensation with the formation of butyraldol [1]. The latter, being an unstable compound, readily gives up water when heated or treated with dehydrating agents and is converted into 2-ethylhexen-2-al (I).



$$\underset{\text{(I)}}{CH_3CH_2CH_2CH{=}\underset{\displaystyle C_2H_5}{\underset{|}{C}}{-}CHO}$$

Raupenstrauch [2] prepared 2-ethylhexenal by heating butyraldehyde with sodium acetate solution or 10% caustic soda solution. Gorhan [3] prepared 2-ethylhexanal from butyraldehyde by heating it with dilute sulfuric acid or fuming hydrochloric acid. Weizmann and Garrard [4] also prepared 2-ethylhexenal by the action of caustic potash solution on butyraldehyde. Batalin and Slavina [5] prepared butyraldol by heating butyraldehyde with 10% caustic potash solution. The butyraldol was converted into 2-ethylhexenal by heating it with sulfuric acid. These same workers also studied the properties of 2-ethylhexenal in greater detail.

Gorin [6], who studied the mechanism of the contact synthesis of divinyl from ethyl alcohol by S. V. Lebedev's method [7], concluded that an intermediate stage in this complex reaction is the condensation of acetaldehyde accompanied by removal of water and formation of crotonaldehyde, which is later reduced to crotyl alcohol, which is then dehydrated to divinyl.

Gorin and Vasileva [8] studied the conversion of n-butyl alcohol with the aid of Lebedev's catalyst. It was shown that in these conditions butyl alcohol forms diethylenic hydrocarbons C_8H_{14}, the carbon skeleton of which corresponds to the skeleton of 3-methylheptane which is formed by their hydrogenation. These hydrocarbons form an isomeric mixture: 3-methylheptadiene-3,5, 3-methylheptadiene-2,4, and 2-ethylhexadiene-1,3. These authors presumed that, by analogy with the conversion of ethyl alcohol to divinyl, the intermediate stages of the reaction should be effected through butyraldehyde, formed by dehydrogenation of butyl alcohol, condensation of butyraldehyde to 2-ethylhexen-2-al, its reduction to 2-ethylhexen-2-ol-1, , and dehydration of the latter to diethylenic C_8H_{14} hydrocarbons.

Thus, the contact synthesis of diethylenic hydrocarbons from primary alcohols by this scheme passes through the intermediate stage of condensation of aldehydes formed by the dehydrogenation of alcohols by the dehydrogenating component of the catalyst.

In order to verify the above scheme for the contact synthesis of diethylenic hydrocarbons from n-butyl alcohol, we carried out experiments on the conversion of butyraldehyde by Lebedev's catalyst and by its dehydrogenating and dehydrating components.

The results showed that both components of the catalyst cause condensation of butyraldehyde and its conversion into 2-ethylhexen-2-al, and under equal experimental conditions the yield of the latter is greater on the dehydrogenating than on the dehydrating component of the catalyst. Butyraldehyde condensation also takes place on a catalyst consisting of a mixture of the components. Thus, the action of Lebedev's catalyst or of its separate components on butyraldehyde is analogous to the action of alkaline or acid reagents, which results in the condensation of butyraldehyde to butyraldol and an unsaturated aldehyde (2-ethylhexenal). The 2-ethylhexenal isolated from the catalytic conversion products of butyraldehyde was confirmed by its boiling point, density, formation of

TABLE 1

Experiments on the Contact Conversion of Butyraldehyde on Lebedev's Catalyst and on its Components

Expt. No.	Catalyst	Temperature	Amount			Fractionation of upper condensate layer. Amounts of fractions (%)					Amount					Yield of 2-ethylhexen -2-al as % of the butyraldehyde	
			Of gas obtained (in liters at 0° and 760 mm) (without air)	Of condensate obtained (in g)	Of water in condensate (%)	Up to 100°	100-150°	150-200°	Residue	Losses	Of 2-ethylhexen -2-al in 150-200° fraction		Of butraldehyde in fraction below 100°		Of reacted butyraldehyde (g)	Per pass	Per amount decomposed
											In g	In %	In g	In %			
1	Component A	400°	7.9	57.3	14.8	23.8	21.4	12.3	40.2	2.3	2.3	41.5	3.4	32.0	74.0	3.0	3.1
2	" B	400	9.3	46.8	42.9	12.4	21.0	17.3	30.6	11.7	0.3	6.2	1.0	19.5	76.4	0.39	0.4
3	" A	350	2.9	69.5	9.3	32.4	12.0	26.6	26.3	2.7	10.0	59.7	14.1	68.9	63.3	12.9	15.8
4	" B	350	3.5	60.7	28.8	32.8	12.2	15.3	30.8	8.9	2.7	40.6	8.0	56.0	69.4	3.5	3.9
5	" A	300	2.0	71.8	9.8	26.5	11.7	31.2	26.4	4.2	12.8	63.3	12.5	73.1	64.9	16.5	19.8
6	" B	300	1.4	70.5	12.5	48.7	4.5	18.6	24.0	4.2	5.6	49.2	16.2	53.9	61.2	7.2	9.1
7	" A	250	0.5	72.2	7.2	35.1	8.2	31.3	24.6	0.8	13.2	63.2	19.0	80.9	58.4	17.1	22.7
8	" B	350	0.3	72.8	4.3	57.7	1.6	24.7	14.9	1.5	9.1	54.1	27.6	68.5	49.8	11.8	15.6
9	Catalyst	375	8.2	61.9	20.4	15.4	43.2	10.5	26.5	4.4	1.4	28.5	1.5	19.6	75.9	1.8	1.9
10	"	300	5.9	67.5	17.8	22.4	31.0	15.1	27.7	3.8	4.1	49.1	7.2	57.6	70.2	5.3	5.8

NOTE. A is the dehydrogenating and B is the dehydrating component of the catalyst.

a semicarbazone with a characteristic melting point, addition of the theoretical amount of hydrogen on hydrogenation, and determination of the carbonyl group content, which agreed with the calculated value for 2-ethylhexanal, with the aid of hydroxylamine.

The formation of 2-ethylhexen-2-al, which has a branched carbon skeleton, from butyraldehyde explains, in accordance with the scheme outlined above, the formation from n-butyl alcohol of C_8H_{14} hydrocarbons with the same carbon skeleton as 2-ethylhexenal.

EXPERIMENTAL

The reaction of contact condensation of butyraldehyde to 2-ethylhexen-2-al was studied on both components of Lebedev's catalyst and on Lebedev's catalyst itself, at several temperatures.

The butyraldehyde used was prepared by catalytic dehydrogenation of butyl alcohol. After being dried, the butyraldehyde was distilled.

B. p. 73.5°; d_4^{20} 0.8074; the content of C_3H_7CHO in the product, determined with the aid of hydroxylamine hydrochloride, was 95.6%.

The contact conversion of butyraldehyde was carried out in a quartz tube 70 cm long, 30 mm diameter, surrounded by an electric heating element. The tube was charged with 200 ml of the catalyst prepared in the form of turnings. The catalyst was activated at 500° for 2 hours before the experiments. One experiment was carried out on each portion of catalyst. In each experiment 100 ml (77.4 g) butyraldehyde was passed through a furnace. The temperature was measured with a thermocouple, the hot junction of which was inserted in the center of the catalyst layer. The liquid and gaseous reaction products were collected in the usual manner. The composition of the gaseous products of each experiment was determined with the aid of the Orsat apparatus.

All the condensates obtained in the experiments were in two layers. The upper oily layer was separated from the lower aqueous layer, dried over calcium chloride, and distilled from a round-bottomed flask with a double bulb dephlegmator; fractions of up to 100°, 100-150°, and 150-200° were taken. The amount of unreacted butyraldehyde was determined in the fraction boiling below 100° with the aid of hydroxylamine hydrochloride. The amount of aldehydes found by the same method in the 150-200° fraction was taken as 2-ethylhexen-2-al. The presence of the latter, as will be seen below, was confirmed in this fraction.

The results of the experiments are shown in Tables 1 and 2.

TABLE 2

Gas Composition in Experiments on the Contact Conversion of Butyraldehyde (in Volume %)

Expt. No.	Catalyst	Temperature	Substances absorbed by alkali	$C_3H_6 + C_4H_8$	C_2H_4	CO	H_2	C_nH_{2n+2}
1	Component A	400°	15.0	14.3	6.2	0.7	58.4	5.4
2	" B	400	1.7	52.4	4.3	0.3	27.6	13.7
3	" A	350	17.1	3.8	2.6	0.0	76.5	0.0
4	" B	350	5.1	38.9	1.4	1.2	53.4	0.0
5	" A	300	18.4	6.5	2.4	0.0	72.7	0.0
6	" B	300	16.5	20.5	3.5	0.0	59.5	0.0
7	" A	250	54.9	1.8	0.0	0.9	42.4	0.0
8	" B	250	22.8	24.1	6.7	0.0	46.4	0.0
9	Catalyst	375	30.4	12.8	2.6	6.3	53.9	0.0
10	"	300	34.1	9.5	2.1	0.3	54.0	0.0

It is seen from the results in Table 1 that the yield of 2-ethylhexen-2-al increased with decreasing temperature. The yield of 2-ethylhexen-2-al was higher on the dehydrogenating than on the dehydrating component of the catalyst.

The gaseous reaction products (Table 2) contained hydrogen formed as the result of dehydrogenation of butyraldehyde condensation products. In addition, unsaturated C_2, C_3, C_4 hydrocarbons were found, formed by the decomposition of butyraldehyde and its condensation products by the action of the high temperature and the catalyst. As was to be expected, the ratio hydrogen/unsaturated hydrocarbons was higher in the gas from experiments on the dehydrogenating than the dehydrating component. The nature of the substances absorbed by alkali, the amounts of which increased with decrease of the experimental temperature, was not established. The amount of carbon dioxide in the gas was insignificant, as was proved by means of baryta water.

Determination of 2-ethylhexen-2-al in the products of the contact conversion of butyraldehyde

To accumulate the reaction products, 3 experiments were carried out on the dehydrogenating component of the catalyst at 300°. In each experiment 200 ml butyraldehyde was passed through the furnace. After each experiment the catalyst was regenerated in a current of air at 500°. The condensates obtained in each experiment were separated from the aqueous layer, combined, dried over calcium chloride and distilled from a round-bottom flask with a four-bulb dephlegmator.

The amount distilled was 401 g, and the following fractions were obtained: 1st, b.p. up to 80°, 46.5%; 2nd, b.p. 80-160°, 14.6%; 3rd, b.p. 160-173°, 15.7%; residue 20.6%; loss 2.6%.

By repeated fractionation of the 160-173° fraction, a narrow fraction was isolated which boiled in the range 172-173°, which corresponded to 2-ethylhexen--2-al [5]; d_4^{20} 0.8549.

Hydrogenation, by Ginzberg's [9] method: 0.3066 g substance added on 54.5 ml H_2 (NTP). Hydrogen number (per one ethylene bond; addition of hydrogen to the aldehyde group may be neglected, as its rate is negligibly low [10]): found 177.75. $C_7H_{13}CHO$. Calculated 177.78. Carboxyl group content (as %, determined by hydroxylamine): found 20.60, 20.73. $C_7H_{13}CHO$. Calculated: 22%.

The semicarbazone consisted of white crystals which melted at 150-151° after recrystallization from methyl alcohol. The fraction with b.p. 172-173°, isolated from the products obtained in the experiments on the contact conversion of butyraldehyde on the dehydrating component of the catalyst, gave a semicarbazone with the same melting point.

Literature data for 2-hexen-2-al: d_4^{20} 0.8528 [4]; semicarbazone, m.p. 150-151° [5].

Thus, the presence of 2-ethylhexen-2-al in the products of the contact conversion of butyraldehyde on the components of Lebedev's catalyst can be considered as established.

SUMMARY

1. The catalytic conversion of butyraldehyde on the dehydrogenating and dehydrating components of Lebedev's catalyst at 250, 300, 350, and 400°, and on the catalyst itself at 300 and 375° was studied.

2. It is shown that in these conditions condensation of butyraldehyde with formation of 2-ethylhexen-2-al takes place. The yield of 2-ethylhexen-2-al decreases with increasing temperature, in the temperature range studied.

3. It is shown that, at equal temperatures, the yield of 2-ethylhexen-2-al is higher on the dehydrogenating than on the dehydrating component of the catalyst.

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INVESTIGATIONS OF CONJUGATED SYSTEMS

LVI. CONDENSATION OF DIENE HYDROCARBONS WITH PROPARGYL ALDEHYDE

A. A. Petrov

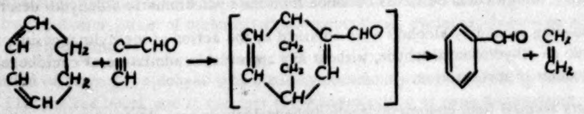
In a series of previous articles, diene syntheses with the aid of butynone were described by the present author [1-6]. Simultaneously with our first papers on the subject, communications by other authors on the condensation of various acetylenic ketones with diene hydrocarbons were published [7, 8]. Nevertheless, the homocyclization of dienes with acetylenic aldehydes of the aliphatic series remained almost unstudied. There is only one paper, which deals with the reactions of tetrolic aldehyde and heptyne aldehyde with divinyl and trimethylbutadiene [9], and patent data [10] which largely do not correspond to reality; therefore, having the opportunity of working with propargyl aldehyde, the author has set himself the task of filling this gap to some extent.

In the present paper the reactions of propargyl aldehyde with divinyl, diisopropenyl, cyclopentadiene, and cyclohexadiene are described. When this aldehyde was heated for a short time with divinyl and diisopropenyl at 115°, $\Delta^{1,4}$-dihydrobenzoic and 4,5-dimethyl-$\Delta^{1,4}$-dihydrobenzoic aldehydes were obtained. The first of these substances is a colorless liquid and the second consists of crystals similar in odor to benzaldehyde.

It was shown by the use of dihydrobenzaldehyde as an example that these substances do not have a conjugated system of carbon-carbon double bonds, as their physical constants are unchanged when they are heated with maleic anhydride. They are readily dehydrogenated on heating with sulfur to form the corresponding aromatic aldehydes. The rings are oxidized and ruptured by permanganate treatment. Oxidation by silver oxide gives acids of more complex structure. The substances react easily with hydrazine derivatives.

Cyclopentadiene reacts with propargyl aldehyde even at ordinary temperatures, with great evolution of heat. The reaction is accompanied by polymer formation. Endomethylenedihydrobenzaldehyde is a liquid with a pungent smell. It resinifies on keeping.

When cyclohexadiene is heated with propargyl aldehyde, benzaldehyde and ethylene are formed. Benzaldehyde was identified by its physical constants and by the melting point of its p-nitrophenyl hydrazone. The ethylene was converted into dibromoethane. Similar removal of the endoethylene bridge was observed in the condensation of cyclohexadiene with butynone [6].



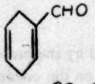
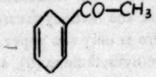
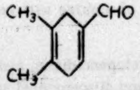
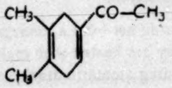
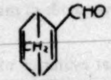
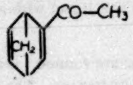
The constants of the hydroaromatic aldehydes obtained are compared in Table 1 with the constants of the analogously constituted cyclohexadiene ketones described in the previous communication.

It is seen from Table 1 that the aldehydes have somewhat higher values for the exaltation of molecular refraction than do the ketones. Their boiling points differ by 12-15°.

A French patent [10] gives only the boiling points, 77-78 and 82-84° (12 mm), for the condensation products of propargyl aldehyde with diisopropenyl and trimethylbutadiene, while for the condensation product of tetrolic aldehyde with isoprene, the boiling point, 90-95° (12 mm), d^{18} 0.962 and n_D^{20} 1.4693 are given. It is obvious that the author of these patents did not have these aldehydes at his disposal, as the constants given differ greatly from those determined by us and given in the above-mentioned English paper (for the substances named in the patent and others of analogous structure) [9].

It was shown in earlier papers (jointly with Sopov [4, 5]) that cyclohexadiene ketones react with organomagnesium compounds to form the corresponding tertiary alcohols which give, on dehydration, hydrocarbons either of the vinylhexadiene or of the aromatic class, according to conditions. The relative yields of the two depend on the structure of the original alcohol and the nature of the catalyst.

TABLE 1

Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR_D		Melting point		
				Found	Calculated	Semi-carbazone	p-nitro-phenyl-hydrazone	2-4-dinitro-phenyl-hydrazone
	80°	1.0230	1.5182	32.04	31.40	204-205	197-198	226°
	94[1,2]	1.0168	1.5150	36.12	36.02	200	204	–
	112-113, m.p. 32.5-33.5	–	1.5176	–	–	230	218-219	233-234
	127.5-128[1,2]	0.9868	1.5118	45.26	45.63	225-226	214-215	234-235
	80	1.0574	1.5218	34.64	33.82	–	–	–
	92[1,2]	1.0362	1.5098	38.71	38.44	–	–	–

In the light of these results considerable interest is attached to the study of the dehydration of secondary alcohols of analogous structure, which could be easily obtained from the hydroaromatic aldehydes described above.

The corresponding secondary alcohols were obtained by the action of methylmagnesium iodide and ethylmagnesium bromide on dihydrobenzaldehyde, without any appreciable admixture of cyclohexene ketones, which are possible by-products in this reaction.

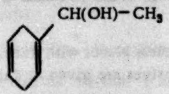
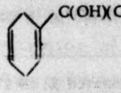
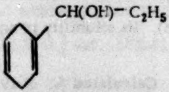
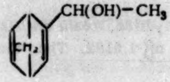
The secondary alcohol from endomethylenehydrobenzaldehyde was obtained in an analogous manner. We must point out here that we did not succeed previously in obtaining a tertiary alcohol from methyl(endomethylene)-cyclohexenyl ketone, as a more saturated ketone was obtained [6].

The action of methylmagnesium iodide on dimethylhydrobenzaldehyde gave a secondary alcohol with an admixture of a carbonyl-containing compound.

In contrast to tertiary alcohols of this series, the secondary alcohols are easily isolated from the reaction mixture and can be distilled in a vacuum without apparent decomposition. These substances are colorless and almost odorless liquids. As Table 2 shows, their molecular refraction values are rather below the calculated values. This was also found for the tertiary alcohols of analogous structure.

The secondary alcohols were dehydrated by distillation over solid alkali, distillation with a small amount of iodine or p-toluene sulfonic acid, distillation with 10% oxalic acid solution, or by the action of acetic anhydride and a drop of H_2SO_4 in the cold. In all cases mainly aromatic hydrocarbons were formed, with small amounts of unsaturated hydrocarbons. Change of the nature of the catalyst had practically no effect on the properties of the reaction product.

TABLE 2

Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR_D	
				Found	Calculated
	103.5°	0.9943	1.5068	37.15	37.53
	97.5	0.9783	1.5012	41.61	42.15
	111-112	0.9778	1.5022	41.73	42.15
	94-96	1.0140	1.5008	39.56	39.95

In this way methylcyclohexadienyl carbinol was converted into ethylbenzene, ethylcyclohexadienyl carbinol into propylbenzene, and methyldimethylcyclohexadienyl carbinol into 1,2-dimethyl-4-ethylbenzene.

It must be pointed out that secondary cyclohexenic alcohols do not split off water in the conditions described above.

Thus, it was established as a result of this study that secondary cyclohexadiene alcohols split off water as easily as the tertiary; however, in the former instance dehydration is accompanied by a greater degree of isomerization, and vinylcyclohexadiene hydrocarbons cannot be isolated as intermediate products.

EXPERIMENTAL

Propargyl aldehyde was obtained by oxidation of propargyl alcohol with sodium dichromate with continuous distillation of the reaction products in a vacuum [11]. The divinyl used was technical grade (99.8%). Di-isopropenyl was prepared by dehydration of pinacol with the aid of acetic anhydride and a few drops of orthophosphoric acid, cyclopentadiene – by depolymerization of technical dicyclopentadiene, cyclohexadiene – by distillation of 1,2-dibromocyclohexane with quinoline.

The condensation of propargyl aldehyde with diene hydrocarbons was carried out in sealed glass tubes in toluene solution at 115° for 2-4 hours, and in the case of cyclopentadiene at room temperature. The reaction products were distilled under vacuum.

The hydrazine derivatives of the hydroaromatic aldehydes were prepared in the usual way: the semicarbazones in aqueous methyl alcohol, p-nitrophenyl- and 2,4-dinitrophenylhydrazones in glacial acetic acid.

The reaction between the hydroaromatic aldehydes and the organo magnesium compounds was also carried out in the usual way. The mixtures were resolved with the aid of magnesium chloride.

The dehydration was carried out in a small Favorsky flask. The hydrocarbons formed were distilled over sodium.

Unsaturated hydrocarbon impurities were removed from the aromatic hydrocarbons by the action of a solution of bromine in acetic acid followed by dilution of the mixture with water and distillation of the hydrocarbon in steam. The amount of unconsumed bromine gave an approximate indication of the unsaturated hydrocarbon content. It was assumed in the calculations that 1 molecule of an unsaturated hydrocarbon takes 2 molecules of bromine. This was the relationship between these reagents established in a previous study [4].

Condensation of propargyl aldehyde with divinyl

From 21.6 g of propargyl aldehyde and 25 g of divinyl in 80 ml toluene, 35.4 g dihydrobenzaldehyde was obtained. The yield on the amount of propargyl aldehyde was 82%. B.p. 184-185° (750 mm). The other physical constants are given in Table 1.

32.60 mg sub.: 92.45 mg CO_2. 21.75 mg H_2O. 0.1540 g sub.: 17.3 g benzene: Δt 0.413°. Found %: C 77.39; H 7.47. M 108.4. C_7H_8O. Calculated %: C 77.74; H 7.47. M 108.3.

The substance forms a semicarbazone very readily. This consists of long colorless plates with truncated edges (from alcohol). The melting points of this semicarbazone and other hydrazine derivatives are given in Table 1.

25.20 mg sub.: 5.605 ml N_2 (24.5°, 752 mm). Found %: N 25.25. $C_8H_{11}ON_3$. Calculated %: N 24.86.

The p-nitrophenylhydrazone was recrystallized from alcohol. Short orange needles.

26.90 mg sub.: 4.057 ml N_2 (24.5°, 755 mm). Found %: N 17.19. $C_{13}H_{13}O_2N_3$. Calculated %: N 17.28.

The 2,4-dinitrophenylhydrazone consists of pale orange needles (from benzene). Its solubility in organic solvents is poor.

9.90 mg sub.: 1.686 ml N_2 (24.5°, 755 mm). Found %: N 19.41. $C_{13}H_{12}O_4N_4$. Calculated %: N 19.44.

After 1 g of dihydrobenzaldehyde was heated for 6 hours with 1 g of maleic anhydride, steam distillation of the reaction mixture gave 0.6 g of a substance with b.p. 80° (20 mm), d_4^{20} 1.0237 and n_D^{20} 1.5182. Thus, the constants of the substance were unchanged.

3 g of dihydrobenzaldehyde was heated for 1 hour with a small amount of sulfur under a reflux condenser. Distillation of the mixture gave benzaldehyde:

B.p. 177-178° (748 mm), d_4^{20} 1.0462, n_D^{20} 1.5462. Literature data [12]: b.p. 178.1°, d_4^{20} 1.0498, n_D^{20} 1.5464.

This substance gave a p-nitrophenylhydrazone characteristic for benzaldehyde, with m.p. 193°, which did not depress the melting point of p-nitrophenylhydrazone from pure benzaldehyde. Considerable depression was produced when the original aldehyde was mixed with p-nitrophenylhydrazone.

5.5 g of dihydrobenzaldehyde was oxidized with silver oxide (prepared from 10 g $AgNO_3$) by heating on a water bath. A little alkali was then added to the solution. The filtered liquid was acidified with 25% H_2SO_4 and the organic acid was extracted by ether in an extractor fitted with a stirrer; this gave 1.8 g of a crystalline acid m.p. 112-113 (from water). It formed colorless plates. The substance contained about 65.8% carbon and 5.4% hydrogen. The molecular weight was about 256. It was not examined further.

From 16.2 g of dihydrobenzaldehyde and a solution of methylmagnesium iodide prepared from 4.3 g magnesium, 15 g (80%) of the corresponding alcohol was prepared. Its constants are given in Table 2. A test with p-nitrophenylhydrazine showed the absence of carbonyl compounds as impurity.

31.50 mg sub.: 88.95 mg CO_2; 27.35 mg H_2O. Found %: C 77.06; H 9.72. $C_8H_{12}O$. Calculated %: C 77.37; H 9.74.

The alcohol was dehydrated in 2.7 g portions by various methods, described in the general section of this paper. In all cases about 70% yield of the same product was obtained, with b.p. 134-136°, d_4^{20} 0.8694-0.8698, n_D^{20} 1.4990-1.5000.

After being heated with maleic anhydride or hydrochloric and acetic acids, and also after bromination in acetic acid, the remaining hydrocarbon (usually about 80% of the original) had physical constants which practically did not differ from the constants for ethylbenzene given in the literature:

B.p. 135-136°, d_4^{20} 0.8652, n_D^{20} 1.4958.

Literature data for ethylbenzene [13]: b.p. 136.2°, d_4^{20} 0.8670, n_D^{20} 1.4959.

From the amount of bromine used (0.19 g) for the bromination of a sample of the substance (1.0 g), its unsaturated hydrocarbon content was about 8%. The bromide isolated from acetic acid was crystallized out. It was not studied further.

Another alcohol was obtained from 5.5 g of dihydrobenzaldehyde, 1.4 g of magnesium, and 9 g of ethyl bromide. The yield was 74%.

33.17 mg sub.: 94.95 mg CO_2; 30.30 mg H_2O. Found %: C 78.11; H 10.22. $C_9H_{14}O$. Calculated %: C 78.23; H 10.21.

Dehydration of this alcohol by p-toluene sulfonic acid gave a hydrocarbon with b.p. 155-156°, d_4^{20} 0.8632, n_D^{20} 1.5010.

Its treatment with bromine solution in acetic acid gave propylbenzene with b.p. 158-159°, d_4^{20} 0.8628, n_D^{20} 1.4926.

The following constants are given for propylbenzene in the literature [13]: b.p. 159.2°, d_4^{20} 0.8620, n_D^{20} 1.4920.

From the amount of bromine used for bromination (0.38 g per 0.8 g hydrocarbon) the unsaturated hydrocarbon content in the original product was about 24%.

Condensation of propargyl aldehyde with diisopropenyl

6.5 g of the aldehyde and 10 g of diisopropenyl gave 12.5 g (73%) of dimethyldihydrobenzaldehyde, with the physical constants shown in Table 1.

52.35 mg sub.: 152.45 mg CO_2; 41.10 mg H_2O. Found %: C 79.47; H 8.79. $C_9H_{12}O$. Calculated %: C 79.37; H 8.88.

The semicarbazone consisted of colorless long plates with gladiate edges. It was recrystallized from aqueous alcohol.

16.90 mg sub.: 3.273 ml N_2 (26.5°, 748 mm). Found %: N 21.72. $C_{10}H_{15}O_2N_3$. Calculated %: N 21.75.

The p-nitrophenylhydrazone was recrystallized from benzene. It formed pale orange crystals.

20.78 mg sub.: 2.764 ml N_2 (25°, 748 mm). Found %: N 15.00. $C_{15}H_{17}O_2N_3$. Calculated %: N 15.49.

The 2,4-dinitrophenylhydrazone was recrystallized from benzene. It formed long orange needles.

24.70 mg sub.: 3.842 ml N_2 (22.5°, 750 mm). Found %: N 17.73. $C_{15}H_{17}O_4N_4$. Calculated %: N 17.71.

From 6.8 g of dimethyldihydrobenzaldehyde and the appropriate amount of Grignard reagent 6.5 g of a mixture of an alcohol and a ketone was obtained. The greater part of the substance boiled at 126-128° (20 mm), d_4^{20} 0.9705, n_D^{20} 1.5085. All fractions of the substance gave a positive reaction with p-nitrophenylhydrazine.

13.55 mg sub.: 39.15 mg CO_2; 12.40 mg H_2O. Found %: C 78.85; H 10.24. $C_{10}H_{16}O$. Calculated %: C 78.90; H 10.59.

The mixture was distilled with 10% solution of oxalic acid without previous separation. The hydrocarbon formed had b.p. 187-189°, d_4^{20} 0.8730, n_D^{20} 1.5030.

After it was treated with bromine as described above, its physical constants practically did not differ from those given in the literature for 1,2-dimethyl-4-ethylbenzene:

B.p. 187-189°, d_4^{20} 0.8750, n_D^{20} 1.5040.

Literature data [13]: b.p. 189.5°, d_4^{20} 0.8741, n_D^{20} 1.5032.

The unsaturated hydrocarbon content in the original substance, from bromination data, was about 17%.

Condensation of propargyl aldehyde with cyclopentadiene

From 15 g of the aldehyde and 20 g of cyclopentadiene, 16.5 g (50%) of endomethylenedihydrobenzaldehyde and 12.5 g of a tarry residue were obtained.

40.30 mg sub.: 117.25 mg CO_2; 24.70 mg H_2O. Found %: C 79.40; H 6.86. C_8H_8O. Calculated %: C 79.97; H 6.73.

All hydrazine derivatives of endomethylenedihydrobenzaldehyde should be prepared from cold solutions. Otherwise resinification takes place. On heating, they char and therefore they do not have sharp melting points.

The p-nitrophenylhydrazone was recrystallized from aqueous alcohol.

15.85 mg sub.: 2.274 ml N_2 (23°, 755 mm). Found %: N 16.55. $C_{14}H_{13}O_2N_3$. Calculated %: N 16.46.

The 2,4-dinitrophenylhydrazone forms red crystals.

8.0 g of endomethylenedihydrobenzaldehyde and Grignard reagent (from 1.9 g of magnesium) gave 6.2 g (70%) of an alcohol. The substance did not give the reaction of a carbonyl compound.

32.60 mg sub.: 94.60 mg CO_2; 25.70 mg H_2O. Found %: C 79.19; H 8.82. $C_9H_{12}O$. Calculated %: C 79.37; H 8.88.

It did not prove possible to obtain a hydrocarbon from this alcohol by dehydration with toluene sulfonic acid or by distillation with 10% oxalic acid solution, as resinification took place. This requires special study.

Condensation of propargyl aldehyde with cyclohexadiene

5.2 g of propargyl aldehyde, 12 g of cyclohexadiene-1,3, and 30 ml of toluene were heated together for 4 hours at 115°. The tubes were cooled to −80° before being opened. A considerable pressure was found during the opening. The gas evolved was partially passed into bromine. After removal of excess bromine by sodium bisulfite, a liquid with the properties of 1,2-dibromoethane remained:

B.p. 130-132°, n_D^{20} 1.5380.

Literature data [14]: b.p. 131.7°, n_D^{20} 1.5379.

Distillation of the liquid part of the reaction mixture under vacuum, and then under normal pressure, gave benzaldehyde as the only reaction product:

B.p. 177.5-178.5°, (745 mm), d_4^{20} 1.0460, n_D^{20} 1.5462.

The p-nitrophenylhydrazone had b.p. 192°.

SUMMARY

1. The homocyclization reaction of divinyl, diisopropenyl, cyclopentadiene, and cyclohexadiene with propargyl aldehyde was studied.

2. It was established that in every instance except the last the reaction products are dihydrobenzaldehyde or its analogs.

3. When cyclohexadiene reacts with propargyl aldehyde, the reaction products are ethylene and benzaldehyde.

4. It was shown that when dihydrobenzaldehyde is heated with sulfur it undergoes dehydrogenation and forms benzaldehyde.

5. A series of secondary alcohols was synthesized by the action of Grignard reagents on the hydroaromatic aldehydes obtained.

6. It was shown that the above secondary alcohols mainly form aromatic hydrocarbons when dehydrated under various conditions.

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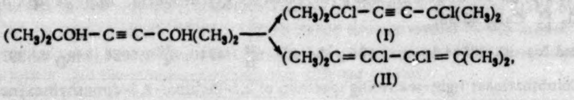
• T. p. = C. B. Translation pagination.

THE ACTION OF CONCENTRATED HYDROCHLORIC ACID ON TETRAMETHYLBUTYNE DIOL. II

A. I. Zakharova and G. D. Ilina

In a previous paper on the action of concentrated hydrochloric acid on tetramethylbutyne diol, one of the present authors [1] showed that two dichlorides are formed in this reaction, with b.p. 65-67° and 80-82° at 15 mm. Difficulties were met in attempts to prove the structure of these dichlorides. It did not prove possible to oxidize the dichlorides by alkaline permanganate solution. At ordinary temperatures the dichlorides were not oxidized, while on heating no oxidation products could be isolated, due to the fact that it became sufficiently evident that in these conditions they were oxidized further to CO_2 and H_2O, but the greater portion of the dichlorides remained unchanged. A noticeable reaction started by the action of metallic sodium on the dichlorides in ether solution, and the dichloride with b.p. 65-67° at 15 mm reacted more vigorously. Chlorine was evidently split off and an unsaturated hydrocarbon was formed, but the latter polymerized in the presence of sodium. The dichloride with b.p. 80-82° at 15 mm did not react with zinc dust in an alcohol medium at all, while its isomer with b.p. 65-67° at 15 mm partly reacted, but the primary product formed could not be isolated, as it was converted into a polymer.

The structure of the dichlorides could not be determined with certainty from these studies. On the assumption that the reaction between acetylene glycol and concentrated hydrochloric acid proceeds according to the equation:



$$(CH_3)_2COH-C\equiv C-COH(CH_3)_2 \longrightarrow \begin{cases} (CH_3)_2CCl-C\equiv C-CCl(CH_3)_2 \quad \text{(I)} \\ (CH_3)_2C=CCl-CCl=C(CH_3)_2, \quad \text{(II)} \end{cases}$$

we presumed that the dichloride with b.p. 65-67° at 15 mm had the diene structure, and the dichloride with b.p. 80-82° at 15 mm was the acetylenic derivative.

Recently R. Ya. Levina and Yu. S. Shabarov [2], with the aim of reacting the ditertiary acetylenic dichloride (I) with an organomagnesium compounds, synthesized both the dichlorides prepared by us, and to prove their structure they used the reaction discovered and developed for the acetylenic monochlorides by T. A. Favorskaya. The latter showed in a number of papers [3] that tertiary acetylenic monochlorides are isomerized into diene derivatives by the action of cuprous chloride and ammonium chloride in an acid medium. R. Ya. Levina and Yu. S. Shabarov subjected the dichloride with b.p. 65-67° at 15 mm to this treatment, and converted 73% of it to the higher boiling dichloride with b.p. 80-82° at 15 mm. On the basis of this result, and also because the higher boiling dichloride did not react with the organo-magnesium compound even upon prolonged heating, these authors concluded that the dichloride with b.p. 65-67° at 15 mm has an acetylenic structure, while the dichloride with b.p. 80-82° at 15 mm is a diene derivative.

Even before the publication of the paper by R. Ya. Levina and Yu. S. Shabarov we decided to return to the question of the proof of the structure of the dichlorides obtained by the action of concentrated hydrochloric acid on tetramethylbutyne diol, by the use of the combinational light-scattering method. It was found that the spectrum of the dichloride with b.p. 65-67° at 15 mm had a strong line which corresponded to the characteristic frequency of the triple bond – 2235 cm^{-1}. No lines were observed in the frequency region characteristic of the double bond. The combinational light-scattering spectrum of the dichloride with b.p. 80-82° at 15 mm contained lines with characteristic frequencies of 1626 and 1666 cm^{-1}, which is evidence of the presence of a double bond in the compound; characteristic triple bond frequencies were absent.

Thus, the results of a spectrographic study of the dichlorides showed, in agreement with the findings of Levina and Shabarov, that the dichloride with b.p. 65-67° at 15 mm should be attributed to the structure of an acetylenic derivative, 2,5-dichloro-2,5-dimethylhexyne-3 (I), while the dichloride with b.p. 80-82° at 15 mm has a diene structure, 3,4-dichloro-2,5-dimethylhexadiene (II).

Before the spectrographic investigation the dichlorides were carefully fractionated and then subjected to 3-fold molecular distillation. It is interesting to note that the dichloride with b.p. 65-67° at 15 mm was obtained in the crystalline state (m.p. 28-29°). Evidently, in this case the dichlorides had been most thoroughly separated*.

The starting glycol – tetramethylbutyne diol – was prepared by A. E. Favorsky's method, by condensation of acetone with acetylene in presence of powdered KOH in ether. The method of carrying out this reaction as used by A. T. Babayan was somewhat modified (see Experimental Section), which made it possible to increase the glycol yield to 80% (instead of 60% [5]). The reaction between concentrated hydrochloric acid and the glycol was carried out in conditions described in a previous paper [1], with the difference that the reaction was carried out with cooling in order to retard the isomerization of the acetylenic to the diene dichloride.

EXPERIMENTAL

Preparation of 2,5-dimethylhexyne-3-diol-2,5. 300 g of powdered caustic potash and 700 ml of dry ether were placed in a thick-walled flask fitted with a rapidly rotating blade stirrer, reflux condenser, and dropping funnel. The mixture was saturated with acetylene for 1 hour while being cooled and stirred. 87 g (1.5 moles) of freshly distilled acetone was added drop by drop for one and a half hours (with a continuous stream of acetylene), after which the stream of acetylene was stopped and another 87 g of acetone was quickly added. The reaction mixture was thoroughly stirred and left 48 hours. After cooling, the reaction mixture was hydrolyzed by water, the ether layer was washed with water, a current of CO_2 was passed through it for 2 hours, and it was dried with potash. After removal of the ether, unreacted acetone, and the acetylenic alcohol, the glycol was redistilled in a vacuum from a flask with a sword-shaped outlet. M.p. 95-97°. The yield was 170 g (80%) calculated on the acetone used for the reaction.

Action of concentrated hydrochloric acid on tetramethylbutyne diol. 284 g (2 moles) of the glycol and 1.5 liters of concentrated hydrochloric acid (d 1.19) were stirred in a round bottom flask for 4 hours with cooling. The dark oily upper layer was separated off, washed with water, and dried with calcium chloride. Two fractions were isolated after fractionation:

1st b.p. 65-67° at 15 mm, 109 g (30.4% on the glycol taken). M.p. 28-29°, n_D^{20} 1.4613, d_4^{20} 1.0118, MR_D 48.58. $C_8H_{12}Cl_2 \vert\!\equiv$. Calc. 46.88.

2nd b.p. 80-82° at 15 mm, 195 g (54.4%), n_D^{20} 1.4940, d_4^{20} 1.0556, MR_D 49.39. $C_8H_{12}Cl_2 \vert\!=_2$. Calc. 47.94.

Combinational light-scattering spectrum of 2,5-dichloro-2,5-dimethylhexyne-3 (I):

234 (2), 338 (2), 421 (1), 464 (1), 577 (4), 607 (4), 701 (5), 846 (3), 918 (3), 1113 (3), 1165 (2), 1208 (1), 1446 (2), 2235 (9), 2295 (2).

Combinational light-scattering spectrum of 3,4-dichloro-2,5-dimethylhexadiene-2,4 (II).

193 (1) 261 (1), 344 (3), 414 (3), 468 (3), 517 (5), 773 (3), 1031 (1), 1170 (3), 1245 (1), 1375 (4), 1437 (4), 1626 (4), 1666 (10).

SUMMARY

It was established by studies of the combinational light-scattering spectra of the two isomeric dichlorides obtained by the action of concentrated hydrochloric acid on tetramethylbutyne diol that the dichloride with b.p. 65-67° at 15 mm has an acetylenic structure – 2,5-dichloro-2,5-dimethylhexyne-3 (I), while the dichloride with b.p. 80-82° at 15 mm is a diene derivative, 3,4-dichloro-2,5-dimethylhexadiene-2,4 (II).

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* Dupont [4], who studied the action of hydrogen chloride on tetramethylbutanediol, obtained one dichloride, with b.p. 62-63° at 15 mm, m.p. 29°. He attributed an acetylenic structure to the dichloride.

INVESTIGATIONS OF COMPOUNDS CONTAINING THREE-MEMBERED OXIDE RINGS

XII. REACTION OF THE ETHYL ESTER OF β,β'-DIETHYL- AND OF THE ETHYL ESTER OF β,β'-DIPROPYLGLYCIDIC ACID WITH ANILINE

V. F. Martynov and V. F. Martynova

As the result of earlier investigations of the reaction between β-disubstituted glycidic acid and aromatic amines [1-5], it was possible to determine the point of rupture of the epoxy ring of glycidic acids and also to develop a new method for the synthesis of indole homologs. The aim of the present study was to investigate the possibilities of this new method of synthesizing the indole structure.

The present general methods for the preparation of indole homologs all have the same general defect: with their aid it is very difficult or quite impossible to synthesize indole derivatives containing radicals more complex than methyl at the 2nd and 3rd carbon atoms.

For example, the method of Fischer [6], which is the most widely known in the literature, is unsuitable in principle for the preparation of such compounds. Indoles are produced by this method by the decomposition of aryl hydrazones of aldehydes, ketones and α-ketonic acids; if it is desired to obtain indoles with substituents at the 2nd and 3rd carbon atoms, the starting substances are usually ketone aryl hydrazones, but indoles of known structure can then only be formed if one of the ketone radicals is a methyl. Closure of the indole ring takes place by the utilization of the carbon atoms of the larger radical. If both radicals should contain several carbon atoms, the synthesis of indoles of a definite structure is impossible, since this rule has not been proved to be generally applicable and it has no definite basis. In such a case the reaction may take two different courses.

The second general method for synthesis of the indole ring with aryl amino ketones as starting materials [7-8], suffers from almost the same defect as Fischer's method. Here the syntheses can be easily effected only on the basis of ketones which contain two or one methyl groups as their radicals, because otherwise the preparation of the corresponding aryl amino ketones is very difficult. The reason for this is that aryl amino ketones are usually synthesized from α-halo ketones, which can be synthesized easily only from ketones which contain, as indicated above, at least a methyl group linked to the carbonyl. If the carbonyl group is linked to radicals containing several carbon atoms, as in ethyl propyl ketone, the synthesis of α-halo ketones of a definite structure becomes very complicated. Similar difficulties arise also in the third method, in which indoles are prepared by intramolecular Claisen condensation of ortho-acyl or ortho-aryl derivatives of alkylanilines [9, 10].

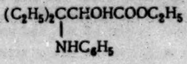
The acyl derivatives of o-toluidine are readily available, but ortho-alkyl substituted anilines containing several carbon atoms in the radical are difficult to obtain, and indoles containing substituents at the 2nd and 3rd carbon atoms can be obtained only from these.

It therefore appeared of interest to investigate the possibilities of the new method of indole ring synthesis for the preparation of 2,3-diethyl- and 2,3-dipropylindoles.

According to our scheme for the conversion of the ethyl esters of α-hydroxy-β-aryl amino acids into indole homologs [1-5], in this case it was necessary to start with the ethyl esters of β,β'-diethyl- and β,β'-dipropylglycidic acids by the addition of aniline at the epoxy ring. It was, of course, to be expected that opening of the epoxy ring of these glycidic acids by the action of aniline would occur with great difficulty because of the protective shielding action of the alkyl groups. In fact, the ethyl ester of β,β'-diethylglycidic acid proved to be very resistant to the action of aniline. When a mixture of aniline was heated with the glycidic ester for 23 hours at 170-180°, the yield of the reaction product, the ethyl ester of α-hydroxy-β-ethyl-β-anilinovalerianic acid (I) was only 17%. An attempt was made to increase the yield by raising the reaction temperature, but a new difficulty arose — some new crystalline compound began to be formed, the amount of which increased with rise of temperature and the time for which the reaction mixture was heated. Eventually, when the reaction was carried out in a flask under a reflux condenser with the reaction mass at the boil, only the crystalline product was obtained. Analysis of this compound suggested that it was the anilide of β,β'-diethylglycidic acid (II).

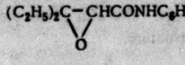
Evidently, at temperatures above 180°, the reaction between aniline and the ethyl ester of β,β'-diethylglycidic acid proceeds in two directions, with the formation of an addition product at the epoxy group, and of the anilide of the original glycidic acid. Above a definite temperature, the latter reaction apparently predominates. The substitution of the ester group by the anilide group proceeds much more rapidly than the opening of the epoxy ring.

The epoxy ring in the ethyl ester of β,β'-dipropylglycidic acid was even more resistant to aniline. The expected addition product was not obtained when a mixture of these substances was heated at 180-185°. The reaction was then carried out as in the preceding instance, with the reaction mixture at the boil; the reaction product was then obtained in the form of a crystalline compound. Investigation showed that this was an anilide. Thus, in the ethyl ester of β,β'-dipropylglycidic acid steric hindrance becomes so great that the epoxy ring completely loses its reactivity to aniline, and the only reaction product is the anilide of β,β'-dipropylglycidic acid (III).

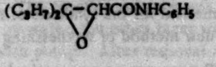


$(C_2H_5)_2\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}CHOHCOOC_2H_5$

(I)

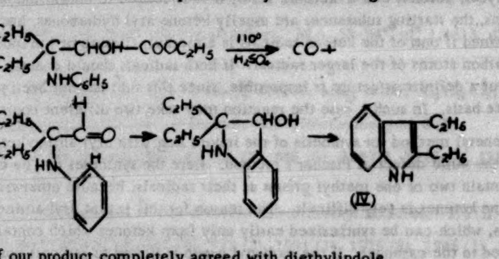


(II)



(III)

The addition product of aniline and the ethyl ester of β,β'-diethylglycidic acid, the ethyl ester of α-hydroxy-β-ethyl-β-lanilinovalerianic acid, was treated with concentrated sulfuric acid on heating. At 110°, as in all the other cases, vigorous evolution of carbon monoxide took place. The other fragment of the molecule could only be 2,3-diethylindole (IV), the formation of which can be represented by the following scheme:



The analytical data of our product completely agreed with diethylindole.

It must be pointed out that the possibility of synthesizing 2,3-diethylindole has been discussed in the literature by A. E. Arbuzov and his co-workers [11]. Their starting material was ethyl propyl ketone phenylhydrazone. The catalytic decomposition of this compound in presence of cuprous chloride gave a compound which, by its analytical data, could have been either 2,3-diethylindole or 2-propyl-3-methylindole. These authors could not, of course, decide on one or the other of these formulas, since the formation of either compound can be considered as equally probable. They claimed, however, that they prepared a single definite compound, and not a mixture of the two possible substances. By a comparison of certain physical constants, for example, the melting points of the picrates of their compound (144°) and of ours (122°), it can now be said that these authors prepared 2-propyl-3-methylindole by the decomposition of the phenyl hydrazone of ethyl propyl ketone.

Thus, the opinion sometimes expressed in the literature that in the indole synthesis by Fischer's method the larger radical participates in the formation of the pyrrole ring is not a general law.

EXPERIMENTAL

Synthesis of the ethyl ester of α-hydroxy-β-ethyl-β-anilinovalerianic acid. A mixture of 17 g (0.1 mole) of the ethyl ester of β,β'-diethylglycidic acid and 27 g (3 moles) of freshly distilled aniline was sealed in a bulb which was heated for 23 hours at 170-180°. The reaction mixture turned slightly yellow, and a slight pressure increase was noted when the bulb was opened. Vacuum distillation yielded 5 g (17%) of a yellowish thick liquid, b.p. 165-167° (3 mm).

0.1051 g sub.: 5 ml N_2 (20°, 764 mm). Found %: N 5.40. $C_{15}H_{23}O_3N$. Calculated %: N 5.20.

Synthesis of the anilide of β,β'-diethylglycidic acid. A mixture of 17 g (0.1 mole) of the ethyl ester of β,β'-diethylglycidic acid and 27 g (3 moles) of freshly distilled aniline was heated to boiling under a reflux condenser on molten Wood's alloy for 10 hours. Vacuum distillation yielded 11 g of a straw-yellow very thick liquid which crystallized rapidly. Repeated crystallization from ligroine gave white scaly crystals, m.p. 114-115°.

0.0873 g sub.: 4.9 ml N_2 (25°, 755.5 mm). Found %: N 6.26. $C_{13}H_{17}O_2N$. Calculated %: N 6.40.

Synthesis of 2,3-diethylindole. 3.9 g of the ethyl ester of α-hydroxy-β-ethyl-β-anilinovalerianic acid was mixed with 15 ml of concentrated sulfuric acid. The reaction mixture was heated over an open flame with stirring. At 100°, bubbles of carbon monoxide began to come off, and at 115° this evolution became very vigorous. The temperature was not raised above 120°. When the gas evolution ceased, the dark reaction mixture was poured into ice, when a brown emulsion separated out. The sulfuric acid was neutralized by alkali, and the whole contents were distilled in steam. The emulsion in the distillate was extracted with ether, and after drying and removal of ether, 1.7 g (68%) of 2,3-diethylindole, of a pale yellow color, was obtained. The crude diethylindole was distilled under vacuum at 118-120° (2 mm). It was a greenish-yellow liquid. The picrate was in the form of yellow needles; it separated out only on dilution with water; m.p. 121-122° after recrystallization from 50% alcohol:

d_4^{20} 1.0205, n_D^{20} 1.5806, MR_D 56.46; calc. 54.95; EMR_D 1.51.

0.1187 g sub.: 8.5 ml N_2 (20°, 765 mm). Found %: N 8.38. $C_{12}H_{15}N$. Calculated %: N 8.09.

Synthesis of the ethyl ester of β,β'-dipropylglycidic acid. The synthesis was carried out by Darzens' method [12]. To a mixture of 57 g of dipropyl ketone (0.5 mole) and 61 g (0.5 mole) of ethyl monochloroacetate, sodium ethylate (0.5 mole) was added with cooling, so that the temperature did not rise above 0°. After the usual treatment, 40 g (40%) of the ethyl ester of β,β'-dipropylglycidic acid was isolated:

B.p. 108-110° (10 mm), d_4^{20} 0.9573, n_D^{20} 1.4337, MR_D 54.44; calc. 54.23.

0.1141 g sub.: 0.2771 g CO_2; 0.1045 g H_2O. Found %: C 66.20; H 10.17. $C_{11}H_{20}O_3$. Calculated %: C 66.0; H 10.00.

Synthesis of the anilide of β,β'-dipropylglycidic acid. 30 g of the ethyl ester of β,β'-dipropylglycidic acid in a mixture with 60 g of freshly distilled aniline (1 : 3) was heated to boiling on Wood's alloy under a reflux condenser for 45 hours. After 2-fold vacuum distillation, 8 g (20%) of a golden-yellow, viscous liquid, b.p. 151-152° (0.5 mm) was isolated. On the next day the substance crystallized out; recrystallization from petroleum ether gave silky needles, m.p. 52-53°.

0.0597 g sub.: 3 ml N_2 (28°, 764 mm). Found %: N 5.40. $C_{15}H_{21}O_2N$. Calculated %: N 5.16.

SUMMARY

1. The reactions of aniline with the ethyl ester of β,β'-diethylglycidic acid and the ethyl ester of β,β'-dipropylglycidic acid were studied.

2. It is shown that with the ethyl ester of β,β'-diethylglycidic acid the reaction proceeds in two directions: the addition of aniline at the epoxy ring, with the formation of the ethyl ester of α-hydroxy-β-ethyl-β-anilinovalerianic acid, and substitution of the ethoxy group by an aniline residue, with the formation of the anilide of β,β'-diethylglycidic acid. The reaction between the ethyl ester of β,β'-dipropylglycidic acid and aniline proceeds in one direction only, with substitution of the ester group by an anilide group, to form the anilide of β,β'-dipropylglycidic acid.

3. The conversion of the ethyl ester of α-hydroxy-β-ethyl-β-anilinovalerianic acid to 2,3-diethylindole has been effected.

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STUDY OF THE REACTION FOR THE CONVERSION OF DIACETONE-2-KETO-L-GULONIC ACID HYDRATE INTO L-ASCORBIC ACID IN ALCOHOL-FREE ORGANIC SOLVENTS

V. I. Veksler and G. E. Shaltyko

Of the many methods for the preparation of L-ascorbic acid (AA) from the hydrate of diacetone-2-keto-L-gulonic acid (HDAKGA), the one most widely studied is in which the reaction is carried out in organic solvents in presence of alcohols [1, 2]. Berezovsky and Strelchunas found that this method gives high yields of AA [2, 3]. They showed that in alcohol-containing mixtures the reaction passes through the stage of formation of an ester of 2-keto-L-gulonic acid, which is converted into AA [3]. The reaction has not been widely studied in organic solvents in absence of alcohols: there are patents [4] and also the results of Berezovsky and Strelchunas, who showed that in a dry inert solvent (chloroform, dichloroethane) the reaction does not take a definite course [2]. It might be thought that the lack of success with the use of inert solvents without addition of alcohols is primarily caused by the slight solubility of hydrogen chloride, which catalyzes the reaction [5, 6], in these solvents.

Our aim was to study the course of the reaction in organic solvents with the addition of substances which are not alcohols by their chemical nature, but which are capable of dissolving approximately the same amounts of hydrogen chloride as are alcohols. It is known that, in addition to alcohols, ethers are good organic solvents for hydrogen chloride [5, 6, 7]. In view of the need to use relatively high-boiling substances, dioxane and dibutyl ether were chosen from this group of compounds. It was confirmed experimentally that these substances are good solvents for hydrogen chloride. At room temperature, solutions were obtained containing 260 g and 146 g of hydrogen chloride in 1 liter of a mixture with dioxane and dibutyl ether respectively.

The study was performed by determinations of the yield of AA in reaction mixtures containing HDAKGA and dichloroethane, to which a solution of hydrogen chloride in dioxane or dibutyl ether was added. For comparison, a parallel experiment was simultaneously performed with a reaction mixture which contained, in addition to HDAKGA and dichloroethane, a solution of hydrogen chloride in 95% ethyl alcohol. The compared mixtures contained approximately equal amounts of hydrogen chloride. The mixtures were heated on a water bath at a definite temperature for 6,6.5, and 9 hours. The results of the experiments are shown in the table.

It is seen from the results in the table that, as a rule, the yield of AA in all the experiments was higher in alcohol-containing mixtures than in mixtures containing dioxane or dibutyl ether as hydrogen chloride solvents.

The yield of AA is determined by the ratio of the rates of two processes: the formation and the decomposition of AA. We found that in the conditions studied there is no actual measurable decomposition of AA. Consequently, the results given in the table represent the relative rates of formation of AA in the reaction mixtures studied.

This difference of the rates of reaction in alcohol-containing and alcohol-free mixtures must be attributed to a different reaction mechanism. In alcohol-containing mixtures, an ester of 2-keto-L-gulonic acid, which is easily converted into L-ascorbic acid [1, 8] is decomposed; it is known, for example, that the methyl ester, in contrast to 2-keto-L-gulonic acid itself, is converted into AA in the living organism [9]. In alcohol-free mixtures, the 2-keto-L-gulonic acid itself and not its ester reacts, and this process is slower.

The different reaction mechanisms, and also the nature of the hydrogen chloride solvent, determine the formation of the reaction by-products. In alcohol-containing mixtures almost white AA is formed, free from tarry impurities. The mixtures containing dioxane give a dirty, tarry, sticky product. It is interesting to note that, according to Berezovsky and Strelchunas [2], a low yield of AA is obtained from dioxane solutions containing alcohol. In experiments in which hydrogen chloride in dibutyl ether was used, the AA was rather purer than in the case of dioxane. As the table shows, addition of water increases the reaction rate, which is in agreement with the findings of Berezovsky and Strelchunas, who demonstrated the favorable effect of water in alcohol-containing mixtures [3].

TABLE

Expt. No.	HDAKGA (g)	Dichloroethane (g)	Reaction conditions		Alcohol-containing mixtures				Alcohol-free mixtures				
			Bath temperature	Time (hours)	Hydrogen chloride solution			Yield of AA (as % of theoretical)	Hydrogen chloride solution				Yield of AA (as % of theoretical
					Amount (ml)	HCl content (g/liter)	Water content (%)		Solvent	Amount (ml)	HCl content (g/liter)	Water content (%)	
1	20	40	75-76°	6	4	253	5	53.5	Dioxane	4	252	0	33.5
2	5	9.1	80-85	6	0.9	176	5	69	Dioxane	0.9	182	5.5	30.0
3	5	9.1	77-78	6	0.9	176	5	49.5	Dioxane	0.9	182	5.5	27.5
4	5	10	76-78	6	1	258	5	74.1	Dioxane	1	260	0	37.7
5	5	10	76-78	6	—	—	—	—	Dioxane	1	260	0	40.7
6	5	10	75-77	6	1	258	5	72.7	Dioxane	1	260	5	57.6
7	5	10	75-77	6	1	258	5	64.2	Dioxane	1	260	5	59.2
8	5	9	78-79	6.5	0.9	155	5	45.2	Dibutyl ether	1.0	146	5	41.2
9	10	20	70-71	9	2.0	155	5	67.5	Dibutyl ether	2.0	~160	0	17.8
10	10	20	70-71	9	2.0	155	5	69.5	Dibutyl ether	2.0	~160	0	29.1
11	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	10	28.2
12	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	10	25.4
13	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	25	71.5
14	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	25	49.2

EXPERIMENTAL**

Starting materials: Dioxane was distilled over metallic sodium, b.p. 99-101°, dibutyl ether was prepared from butyl alcohol [10], b.p. 139-142°, hydrogen chloride was dried by passing it through sulfuric acid, the HDAKGA was 98.5% pure (calculated as the hydrated substance).

Determination of the relative rate of formation of AA was carried out by heating of the reaction mixture on a water bath under a reflux condenser with vigorous stirring. The experiments with alcohol-free and alcohol-containing mixtures were carried out in parallel, under the same conditions. The yield of AA was determined by analysis of the reaction products by iodine titration in presence of starch. In most of the experiments the reaction product was separated by suction, thoroughly washed with a chloroform-alcohol mixture (4 : 1), dried, and analyzed. In some experiments the reaction mixture was analyzed direct without isolation or purification of the AA.

Determination of the rate of decomposition of AA. 0.1000 g samples of AA were heated for 6 hours on the water bath (76-78°) with a mixture of 1 ml of dichloroethane and 0.1 ml of hydrogen chloride solution in dioxane (260 g hydrogen chloride in 1 liter). After the heating, the amount of L-ascorbic acid was determined by iodine titration, and was 102.9 and 102.4% of the original amounts.

SUMMARY

It is shown that the conversion of the hydrate of diacetone-2-keto-L-gulonic acid into L-ascorbic acid is slower in mixtures in which ethers are used as solvents for hydrogen chloride than in alcohol-containing mixtures.

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** M. F. Galina and M. P. Benyamin participated in the experimental work.

CHEMISTRY OF CUPRAMMONIUM SOLUTIONS OF CELLULOSE

VI. ALCOHOLATE COPPER ATOMS IN CUPRAMMONIUM SOLUTIONS OF CELLULOSE

S. N. Danilov and M. G. Okun

A number of studies [1, 2, 3] of cuprammonium and cupriethylenediamine solutions of polyhydric alcohols and cellulose led to the widespread acceptance of the view that cuprammonium solutions of cellulose contain the compounds:

$$\left\{[(C_6H_8O_5)_2Cu]\ \ [Cu(NH_3)_4]\right\}_n$$

and

$$\left\{[C_6H_7O_5Cu)_2]\ [Cu(NH_3)_4]\right\}_n$$

A characteristic feature of these formulas is the presence of an anion containing copper atoms in alcoholate form, and a cation which is also linked in alcoholate structure to the cellulose, and which is a base, the copper tetramine complex. The interrelationships of copper, alkali, and Rochelle salt in Fehling's solution [1, 2] are often explained in terms of the copper alcoholate derivative of Rochelle salt.

The well-known precipitates formed by the action of caustic alkalies on cuprammonium solutions of cellulose, which are known in the literature as Normann's compounds [4], are given the composition: $(C_6H_8O_5)_2CuNa_2$ by analogy with the formula attributed [1] to sodium cupriglycerates: $(C_3H_5O_3Cu)Na \cdot H_2O$. Hess and his co-workers [3] considered that if smaller amounts of caustic soda were added, cuprammonium solutions of cellulose might contain the compound $(C_6H_7O_5Cu)Na$ (soluble). From their studies of the optical rotation of cuprammonium cellulose solutions they concluded that the angle of rotation (to the left) increases with increasing copper concentration and the subsequent increase in the concentration, of a copper-cellulose compound of high rotatory power in the solutions. The increase in the angle of rotation is particularly great if caustic soda is added to the cuprammonium solution of cellulose; the above-mentioned soluble copper-sodium cellulose derivative is then formed in the solution.

The existence of these compounds in cuprammonium solutions is confirmed, in the view of some authors, in addition to the above considerations, particularly by the experiments of Hess and Messmer [5] on the electrophoresis of cuprammonium solutions of cellulose and polyhydric alcohols.

These authors found that without addition of caustic soda to the solutions copper is apparently displaced only toward the cathode, and in presence of caustic soda, toward the anode. In their opinion, in absence of alkali the copper (the cellulose-copper anion) should also be displaced toward the anode. It is stated in their paper that in the anode limb of the electrophoresis cell cellulose separated out rapidly, which was explained by loss of copper from the anode space, as copper is displaced toward the cathode more rapidly than the anionic cellulose-copper complex is moved toward the anode. In the presence of caustic soda, the sodium ions are moved more rapidly toward the cathode, so that the complex ion is not decomposed and the transport of the copper-cellulose anion from the cathode becomes noticeable. They extended their experiments to solutions of glycerin, mannitol, sucrose, and other sugars, which are analogous to cellulose solutions, and obtained the same results throughout.

As electrolysis experiments are usually cited as proof of the presence of chemical compounds of the alcoholate type in cuprammonium solutions of cellulose, namely, an alcoholate copper atom in the anionic cellulosic part of the compound, it was important, for an understanding of the nature of cuprammonium solutions of cellulose, to make a closer study of the electrolysis (electrophoresis) of these solutions of cellulose and its derivatives, other sugars, and polyhydric alcohols.

Numerous electrolysis experiments were performed, first without separation of the anode and cathode spaces, and then with the use of a separating membrane, solutions of cupric hydroxide in ammonia being compared with cuprammonium solutions of cellulose, oxycellulose, methylcellulose, hydroxyethylcellulose, alginic acid, glucose, sucrose, glycerol, sorbitol and Fehling's solution. Ammonia solutions (15%) with and without caustic soda additions were used as the upper layer of electrolyte. In experiments with the apparatus in which the anode and cathode spaces were not separated, solutions of ammonia and a number of salts were used for the upper electrolyte layer, in order to raise the conductivity of the solution to the limits reached by the addition of caustic soda to the solution. Hess and Messmer assumed that movement of the liquid to the anode took place in presence of caustic soda. Our experiments showed that increase of the conductivity of the upper layer did not affect the phenomena which took place by the action of an electric current on cuprammonium cellulose solutions. It was found in all the experiments with different cuprammonium solutions that copper was deposited only on the cathode, there was no movement toward the anode, and no copper was found in the anode liquid.

It is therefore necessary to amend the conclusions drawn by Hess and Messmer. Our experiments on the action of an electric current on the solutions give reason to believe that cuprammonium solutions of polyhydroxy compounds do not contain alcoholate copper atoms in the presumed compounds.

The same conclusion must be drawn on the basis of our experiments on the action of ionites (anionites and cationites) on cuprammonium solutions of cellulose and other polyhydroxy compounds. Copper was taken up quantitatively by the cationites in all cases, while anionites produced no changes in the solutions. If, however, in agreement with the Traube-Hess hypothesis, cuprammonium cellulose solutions contained any at all stable cupricellulose anions, these might be expected to be taken up by the anionites.

Our results, which contradict the widely accepted [6] views of Traube and Hess, require other hypotheses to account for the interaction between the components of cuprammonium cellulose solutions.

In his determinations of the composition of cuprammonium cellulose compounds, K. Hess [3] attempted to prove the validity of the false hypothesis concerning the small cyclic molecules of high polymers. K. Meyer and H. Mark [7] considered these solutions in the light of their erroneous micellar hypothesis, which was persistently applied by T. Lieser [8] to account for the composition and properties of cuprammonium solutions of cellulose and the solution process itself, even after other workers [9] proved that they were molecular and not micellar in nature. In the work of one of the present authors [10] cuprammonium cellulose solutions were described as consisting of large cellulose molecules, which build up the cellulose fiber itself. The coagulation of the solutions by the action of salts was regarded as precipitation of cellulose in consequence of binding of the salt ions by the cuprammonium hydroxide, resulting in salting out of cellulose. Possibly, the salts coagulate the hydrophobic copper hydroxide, which is partly in the colloidal state. It was also doubted whether the sodium-copper precipitates (Normann) and cellulose cuprammonium compounds (Traube and Hess) have the composition ascribed to them in the literature.

Recently Arkhipov pointed out the unsatisfactory nature of the formulas in which alcoholate copper atoms are contained in the glucose residues in cellulose. In addition to the continuing studies of cuprammonium cellulose solutions by their rotation of the polarization plane (Arkhipov [11], Reeves [12]), other methods are also now in use (condictimetric[13], spectrophotometric, potentiometric [14]). However, the problem of the composition and structure of the presumed cuprammonium cellulose compounds has not yet been reliably solved. Different and often contradictory opinions have been put forward concerning the nature of cuprammonium cellulose solutions. According to some views [15], the solution of cellulose in ammoniacal copper hydroxide is a purely adsorptional process of colloidal peptization, but this reflects only one side of this complex phenomenon. Some authors [16] consider not only the copper amine complexes but also their compounds with cellulose to the complex compounds, but there are no adequate data or convincing analogies in support of this conclusion. Reeves [13] supports the view that cuprammonium hydroxide is added on to the glycol grouping of polyhydroxy compounds (carbon atoms 2 and 3 in the glucose residues of cellulose) but this requires more direct proof.

There is probably no special difference in principle between the reactions of cellulose with caustic soda and with cuprammonium hydroxide, the composition of which may be expressed by the formula $[Cu(NH_3)_m(OH)_2]$, although it seems that in solutions the tetramine complex predominates, as was pointed out by D. P. Konovalov [17].

While cuprammonium hydroxide is a typical unstable complex base of variable composition, we believe it more probable that cellulose-cuprammonium compounds should be considered not as complexes but as molecular compounds, analogous to alkali compounds of cellulose: $[(C_6H_{10}O_5)_x(NaOH)_y(H_2O)_z]_n$ – for alkali cellulose, and $\{(C_6H_{10}O_5)_x \cdot [Cu(NH_3)_m(OH)_2]_y(H_2O)_z\}$ – for the cuprammonium cellulose compound.

EXPERIMENTAL

The Experimental Section describes studies of the electrolysis (electrophoresis and electroosmosis) of cuprammonium cellulose solutions and (for comparison) of ammoniacal solutions of copper hydroxide, and also chromatographic investigations of the same solutions.

Starting substances and solutions. Cotton cellulose from a single batch with the following characteristics: alpha-cellulose 98%, as 0.3%, copper number 0.3, moisture 0.3. Oxycellulose was prepared by A. M. Nastyukov's method, by permanganate oxidation of cellulose and had: acid number – 27 and 31 ml of 0.01 N sodium hydroxide solution, copper number 10-20, carboxyl group content from 0.7 to 0.9%; it was easily ground to a powder. Methylcellulose, prepared from alkali cellulose by the action of dimethyl sulfate, contained 9.8-10.1% methoxyl groups. Hydroxyethylcellulose was prepared in the usual way from alkali cellulose in presence of ethylene oxide at –5°, and was isolated by precipitation by alcohol. Alginic acid was isolated from 10% aqueous sodium alginate solution by an alcoholic acetic acid solution, washed with alcohol, and dried in a vacuum.

Crystalline copper hydroxide, obtained from copper sulfate by the action of ammonia and caustic soda (by Peligot's method) was used in the experiments. Moist copper hydroxide was used. The copper content was determined electrolytically (a sample of 0.5-1 g of the hydroxide was dissolved in 25% sulfuric acid and a current of 3 A was passed for 40-60 minutes at 50° with vigorous stirring).

A weighed sample of the copper hydroxide was mixed with water in vessel of accurately determined size, a weighed amount of the cellulose and the other substances under investigation was added, and ammonia was then added rapidly, the whole capacity being used to displace the air. The liquid was then shaken for 1.5-2 hours. The solutions were separately prepared for each experiment and stored for one day.

The ratio of the components with which solution takes place is determined by the properties of the cellulose. The solution compositions for 0.5 to 4% by the properties of the cellulose and other polysaccharides were determined experimentally. For the preparation of more concentrated solutions, shaking alone is insufficient, and vigorous stirring is needed. The ammonia concentration in all the experiments was 15% of the weight of the solution. The complete dissolution of the cellulose and copper hydroxide was checked microscopically.

Excess ammonia was used for dissolving the copper hydroxide. There is no stoichiometric ratio between cellulose and copper in the solution: the higher is the cellulose concentration per unit volume of the solution, the lower is the relative concentration of copper required for solution to take place. Lower concentrations of copper are needed to dissolve oxycellulose, cellulose ethers, and alginic acid, than to dissolve cellulose.

1. Action of an electric current

Two series of experiments were carried out to determine the chemical nature of cuprammonium cellulose solution by use of the migration of charged particles and ions in an electric field: 1) electrophoresis in which the anode and cathode spaces were not separated from the solution under investigation; 2) electrophoresis with a separating membrane. Direct current at 110 V was used, and the current was varied between 30 and 200 mA.

1) Electrophoresis without separation of the anode and cathode spaces. As the determination was hindered in U-tubes without taps by some mixing of the layers, resulting in an indistinct separation boundary, apparatus of the following construction was used for the electrolysis: the tube was fitted with two taps with cross-sections equal to that of the tube limbs, and had, at its lower part, an upward branch with a tap for adding the solution for investigation; both limbs of the tube were graduated so that the rate of movement of the colored layer could be measured. As the passage of current heats the liquid considerably, thus causing the layers to mix rapidly, the apparatus was placed in a thermostat cooled by running water. The electrodes were platinum plates 5 x 30 mm, and 0.2 mm thick. To prevent mixing when the apparatus was filled, the solution of electrolyte was added to the limbs of the U-tube from above with the taps closed, and the platinum electrodes were then lowered in. The investigated solution was then gradually added through the branch tube, the taps were opened, and the electrolyte was displaced upwards until the electrodes were immersed in it. The duration of each experiment was 1 to 3 hours; water was also electrolyzed, and this was accompanied by evolution of gas bubbles on the electrodes. To prevent mixing of the liquid, the evolution of bubbles must be slow. The most typical of the numerous experiments are described.

a) In the first series of experiments the upper electrolyte layers was 15% ammonia solution, and, in parallel experiments the same solution with the addition of 1% caustic soda per 100 parts of the ammonia solution (15%). The caustic soda was added to increase the hydroxyl ion content, because of the available data concerning sodium-cuprammonium cellulose complexes, of which the so-called Normann compounds are an example, and also because of the polarimetric investigations carried out by K. Hess and his co-workers on cuprammonium cellulose solutions in presence of caustic soda. The height of the layer of the investigated solution was 30 mm. The role of the caustic soda may be to increase the conductivity of the solution.

When 1% solution of ammoniacal copper hydroxide was used, which is presumed to contain copper ammine complexes, the current of electricity caused the colored mass of solution to move toward the cathode, where copper was then deposited from the solution; no changes were observed in the anode limb, and the upper layer remained colorless. Both in this and in other experiments the presence of caustic soda in the upper layer of 15% ammonia solution mainly favored the disappearance of the boundaries between the layers in the cathode and anode spaces (by intensified electrolysis of water).

Similar effects accompanied the electrophoresis of 1% cuprammonium cellulose solution: the boundaries between the layers gradually became indistinct, especially in presence of caustic soda. When the cellulose concentration in the solution was increased (2.4%), the boundaries were retained longer, especially in absence of caustic soda, but the upper layer in the cathode space became blue without disappearance of the boundary between the layers, although the boundary rose by several millimeters; copper was deposited at the cathode. White flakes of cellulose (containing no copper) were deposited in the anode space at the boundary.

When 4% cellulose solution was used, in presence of caustic soda in the upper layer, the cellulose flakes which formed at the boundary slowly moved to the anode, but did not reach it even in experiments lasting many hours. The addition of 1% caustic soda solution (a total of 0.5 g caustic soda) to 2% cellulose solution did not change the observed effects, although the layers mixed more quickly.

The electrophoresis of hydrophilic cellulose ethers in such conditions was also studied, and also, to elucidate the role of carboxyl and hydroxyl groups, the electrophoresis of specimens of oxycellulose, alginic acid, Fehling's solution, sugars, and polyhydric alcohols. For example, it was found that the electrophoresis of 4% methylcellulose and hydroxyethylcellulose solutions (1.75% copper in the solutions) differed little from the experiments described above: copper was deposited at the cathode, the anode liquid turned blue, and , in the electrophoresis of hydroxyethycellulose, in presence of caustic soda, flakes of hydroxyethylcellulose (free from copper) appeared at the boundary due to the solution becoming poorer in copper. Thus, no effects were observed which might prove the presence of copper in the anions of cuprammonium cellulose complexes.

In the electrolysis of cuprammonium solutions of oxycellulose, white flakes were deposited more rapidly in the anode limb, but these flakes also did not contain copper; no copper was deposited at the anode. The oxycellulose formed at the boundary between the two layers was retained at the boundary and then rose toward the anode without reaching it, but the boundary itself fell by 7 mm in 3 hours. When alginic acid was used, the liquid rose considerably in the anode limb and fell in the cathode limb (by 23 mm). The electrophoresis of 4% sodium alginate solution did not differ from the electrophoresis of the cuprammonium complex.

Solutions of tartaric acid in ammoniacal copper hydroxide solution or mixed with copper sulfate showed similar effects under the action of an electric current. Metallic copper was formed at the cathode, while the boundary between the solution moved toward the anode if the upper layer contained caustic soda. The same was observed in the electrolysis of Fehling's solution but the anode boundaries did not move. The experiments showed that movement of the solutions toward the anode was more pronounced when caustic soda was present in the upper layer, and particularly if the molecules of the substance contained carboxyl groups (as in oxycellulose); this is apparently caused by changes in the conductivity of the solutions and possibly to increased electric charge of the substance.

When an electric current acted upon cuprammonium solutions of glucose, sucrose, glycerol, and sorbitol, the colored solution easily diffused into the electrolyte, which may have been caused by the low viscosity of these solutions. The separation boundary between the solutions moved toward the cathode, where metallic copper was formed. These effects did not differ from those observed in ammoniacal solutions of copper hydroxide.

Thus, this series of experiments did not provide confirmation of the hypothesis put forward by Traube and Hess [2, 3] concerning the presence of alcoholate copper in cuprammonium solutions of polyhydric alcohols, sugars, cellulose and its ethers, oxycellulose, tartaric acid, and Fehling's solution.

b) In the second series of experiments (without separation of the anode and cathode spaces) a study was made of the part played by electrolytes in the solutions in relation to the addition of caustic soda, and in particular the role of electrical conductivity. The following were added to 15% ammonia solution in the upper layer: lithium hydroxide, as an analog of sodium hydroxide, but differing in the greater hydration of the lithium ion, in 2.5% concentration (conductivity $\kappa \cdot 10^4 = 1416$); 5% solution of potassium hydroxide ($\kappa \cdot 10^4 = 1464$); 5% solution of caustic soda, the conductivity of which is close to that of the above solutions ($\kappa \cdot 10^4 = 1954$). Salts were also used which could partially give up their anions to the ammine copper complex: 5% ammonium sulfate solution ($\kappa \cdot 10^4 = 552$), 5% lithium chloride solution ($\kappa \cdot 10^4 = 733$), 5% sodium chloride solution ($\kappa \cdot 10^4 = 672$), 15% ammonia solution ($\kappa \cdot 10^4 = 10$). Each electrophoresis experiment with cuprammonium cellulose solution (4% cellulose) and the various electrolytes was carried out three times, and the same effects were observed in each.

The experiments showed that increased conductivity of the solution by use of 15% ammonia solution with the above salt additions as electrolytes (from $\kappa \cdot 10^4 = 10$ for ammonia solution to $\kappa \cdot 10^4 = 700$ when the salts were added) did not result in any special changes in the action of the current on cuprammonium cellulose solution. The solution, as was the case when an ammoniacal electrolyte was used, moved a little in the direction of the cathode, where metallic copper was formed; the cathode liquid turned blue. Cellulose was formed in the anode limb, but the separation boundary remained stationary.

The effect of additions of caustic alkalies to 15% ammonia solution was rather different. In all the experiments in which alkalies were added the boundary rose in the anode limb, but without a corresponding fall of the boundary in the cathode limb. The liquid turned blue near the cathode, and metallic copper was formed at the cathode. The special effect of alkalies on the electrophoresis of cuprammonium solutions is apparently due to the hydroxyl ions of the alkalies and their high conductivity.

2) Electrophoresis with a separating membrane. In order to prevent diffusion of the solution into the upper layer of electrolyte, experiments were performed in which the anode and cathode spaces were separated by porous ceramic membranes with 1.83 - 2μ pore diameter. The apparatus consisted of two porous ceramic beakers, one inside the other, placed in a small glass crystallizing dish. Various arrangements of electrode positions and ways of placing the electrolytes and test solutions into the three spaces — the central and the two annular — were investigated, as shown in the table.

The studies performed in porous vessels on ammoniacal copper hydroxide and cuprammonium cellulose solutions showed that the copper ammine complex passed freely through the porous walls with pore size of about 2 μ, and metallic copper was deposited on the cathode, and that electrophoresis of cuprammonium cellulose solutions took the same course both in presence of ammoniacal electrolyte and after addition of caustic soda to the latter.

When cuprammonium cellulose solution was the anode liquid, cellulose was deposited on the walls of the porous vessel in the anode space, apparently as the result of decompositon of the ammine copper complex, as copper was formed on the cathode.

When the anode space was situated between porous walls, no cellulose appeared in the outer chamber in the anode space, even in traces, but it was deposited on the inner surface of the porous wall, while copper was deposited at the cathode, and there was some loss of the anode liquid. When the electrolyte was completely separated from the cuprammonium cellulose solution which was between the two porous walls, the cellulose particles did not penetrate through the porous walls of the vessels. These experiments also did not confirm the presence of copper in the anion of the cellulose complex.

II. Interaction between cuprammonium cellulose solutions and ionites

In order to obtain data which might help the clarification of the chemical nature of cuprammonium cellulose solutions, the ion exchange of such solutions on cationites and anionites was studied. If cuprammonium cellulose solutions contain compounds of cellulose with a cuprammonium complex base, and copper atoms participate in complex formation in the anionic and cationic parts of the molecule, such ions might be expected to be taken up by anionites and cationites. It is obviously necessary for both ions to have adequate stability and to be capable of being absorbed. Copper may be absorbed from solutions, for recovery purposes, by means of H-permutites and other cationites.

The following Wofatites were used in our experiments: the weakly acidic cationite C, the strongly acid cationites D and KS, the weakly basic anionites M, MP, MMG-1, TN, and the strongly basic anionite PEK, in static and dynamic conditions. In the static experiments, a weighed sample of the anionite was placed direct in the solution to be studied, from which the ions were to be removed, and the solution was shaken intermittently or continuously. In the dynamic experiments, the cationite or anionite was wetted with water and placed in a column 200 mm high and 20 mm diameter, with a porous bottom, and the solution was then added. In order to obtain an even layer of ionite in the column, it was sufficient to tap the walls. The cationites were washed with 50 ml of 12% hydrochloric acid, the first portions being passed in a fine jet and the rest drop by drop, and were then treated with 250 ml of 5% standard hydrochloric acid added dropwise. Periodic determinations of the acid were then made in samples (5-10 ml) to determine whether the cationite was ready for the experiment, when the concentration of the effluent acid was equal to that of the original acid. The anionites were washed with 50 ml of 12% soda, and then with 250 ml of 5% standard soda solution. The conditions of treatment were analogous to those for the cationites. The ionites prepared in this way were washed for a long time (3-4 days) with distilled water; the first portions of water were added in a fine jet, and the rest drop by drop. Methyl orange and phenolphthalein were used as indicators.

1 and 2% cuprammonium cellulose solutions, and, for comparison, 0.5 and 1% solutions of copper hydroxide in ammonia, were studied.

Electrophoresis with Separating Membrane

Experiment number	Arrangement of electrodes and liquids			Effects in the spaces	
	Central space	Inner ring	Outer ring	Cathode	Anode
1	Cathode – 15% ammonia solution	Solution of copper hydroxide in ammonia	Anode – 15% ammonia solution	Cathode liquid turns blue, copper deposited on cathode	No changes
2	Anode – cuprammonium cellulose solution	Cathode – 15% ammonia solution	–	Ditto	Cellulose deposited
3	Cathode – cuprammonium cellulose solution	Anode – 15% ammonia solution	–	Copper deposited on cathode	No changes apart from partial displacement of the anode liquid into the cathode space
4	Cathode – 15% ammonia + 1% caustic soda solution	Anode – cuprammonium cellulose solution	–	Cathode liquid turns blue, copper deposited on cathode	Cellulose deposited
5	Cathode – cuprammonium cellulose solution	Anode – 15% ammonia + 1% caustic soda solution	–	Copper deposited	Displacement of anode liquid into cathode space
6	Anode – 15% ammonia + 1% caustic soda solution	Cuprammonium cellulose solution	Cathode – 15% ammonia + 1% caustic soda solution	Liquid turned blue, copper deposited	Part of the anode liquid displaced into central ring
				Cellulose deposited on inner wall of larger porous vessel	

1) Behavior of ammoniacal copper hydroxide solutions on ionites. a) Cation exchange. A known weight of the solution (10, 20, 25, and 50 g) was passed through the cation layer slowly from a buret; the solution flowed out of the column drop by drop; nitrogen, carefully purified to remove oxygen, was first passed through the column to prevent oxidation of ammonia in presence of copper. Copper and ammonia were completely absorbed from the solutions. The absence or presence of copper in the effluent was checked by a drop reaction with benzidine and KBr with the formation of a blue color on the filter paper; the presence of ammonia was detected with phenolphthalein.

To establish the way in which the ionite reacted with the solution, the reversibility or irreversibility of the absoprtion was determined by washing the column with water and salt solutions (20% solutions of calcium chloride and ammonium nitrate, or 12% hydrochloric acid).

cat.

It was shown by prolonged washing of the anionite with water (1500 ml) that irreversible sorption took place in the reaction with ammoniacal copper hydroxide solution, and this was confirmed by quantitative determinations, both when 10 g of 0.5% (copper content) and 10 g of 1% solutions of ammoniacal copper hydroxide solutions were used. Copper was not washed away from the cationite at all, while ammonia was retained in the cationite, despite prolonged washing, in amounts of 22.5 and 23.7 moles (for 0.5 and 1% solutions respectively) per gram-atom of copper.

Washing by electrolytes was used in experiments in which different amounts (10-50 ml) of an ammoniacal solution of copper hydroxide was passed through the cationite layer, the solution being completely absorbed. Various volumes of 20% solutions of calcium and aluminum salts were used to extract the absorbed copper, and the effluent liquids were analyzed electrolytically for copper (after being made alkaline with ammonia). With a large excess of the salt solutions (400 ml $CaCl_2$ and 600 ml $Al(NO_3)_3$ per 25 g of solution) up to 99.9% of the copper was washed out, which confirms that ion exchange and not mere sorption took place. It is obvious that 1.5 times more calcium chloride than aluminum nitrate was needed to remove the same amount of copper. The copper and ammonia are more conveniently removed by concentrated hydrochloric acid (12%), as large volumes of salt solutions are needed – moreover, when salts were used, the cationites could not be used for further experiments. Without giving tabulated results, we note that 50 ml of hydrochloric acid solution is sufficient to remove to to 99% of the copper.

b) Anion exchange. When the ammoniacal copper solution passed through an anionite column, it flowed through without change of composition, which indicated absence of ion exchange.

2) Ion exchange of cuprammonium cellulose solution. a) Cation exchange. The experiments were carried out both in dynamic and static conditions. A 10 g sample of the solution was passed through the cationite, previously freed from air by a stream of nitrogen, in an atmosphere of which the whole experiment was carried out. Lumps of cellulose were deposited on the cationite surface, while copper and ammonia were taken up by the cationite. No copper was found in the effluent liquid. A parallel experiment in static conditions was performed for comparison. The prepared cationite was added to 10 g of cuprammonium cellulose solution in a glass bottle and shaken. The liquid and lumps of cellulose were decanted from the cationite, which was transferred to an adsorption column, where it was washed first with water and then with solutions of the above salts or hydrochloric acid; it was found possible to remove up to 99.6% of the copper which was contained in the solution by these reagents, while water did not wash out copper ions.

These experiments showed that copper and ammonia are absorbed from cuprammonium solution as the result of ion exchange, and not mechanically or by molecular adsorption.

b) Anion exchange. As fine-grained anionites were used (grain size 0.1-0.2 mm) the viscous cuprammonium solution of cellulose could not pass through them, as the use of vacuum or pressure might favor loss of ammonia, and therefore the cation exchange experiment was performed in static conditions. The anionite was added to a known amount of the solution, and the contents were shaken for 1-1.5 hours. The amount of copper, determined electrolytically before and after the anionite treatment, did not change, and the solution was generally unchanged. No ion exchange took place in these conditions, which is contrary to the views of Traube and Hess concerning the presence of copper in the anion of the cellulose cuprammonium complex.

During prolonged interaction of the solution with the M and MMG-1 anionites (during 5-7 days) it was noticed that the solution decomposes with absorption of copper and evolution of cellulose due to insufficient alkalinity of these anionites. With the use of PEK anionite the composition of the solution did not change during prolonged interaction.

3) Ion exchange of cuprammonium solutions of salts and hydroxy-acids. Cation exchange of the following was studied on cationites and anionites: a) cuprammonium solutions of glucose, Rochelle salt, and tartaric acid; b) a mixture of tartaric acid and copper sulfate; and c) ordinary Fehling's solution. In all cases copper was absorbed by the cationite and the solution became colorless.

In experiments with anionites, cuprammonium solutions of glucose, Rochelle salt, and tartaric acid were unchanged. Fehling's solution and the mixture of tartaric acid and copper sulfate were decolorized and copper hydroxide was precipitated as the result of absorption of the sulfate ions and tartaric acid. The experiments were performed in static conditions. The ion exchange medium was added to the solution which was shaken for some time, and the solution was then decanted from the ionite. The color changes which took place in the solutions in presence of cationites were measured by means of a differential electrophotocolorimeter with two photoelectric cells. Uranium glass was used as a light filter. The color of the original solution was compared with the color of the solution decanted from the ionite. For the sake of brevity, tabulated results are not given.

SUMMARY

1. There is no foundation for the view of Traube and Hess that cellulose-cuprammonium compounds are the products of consecutive interaction, with evolution of water and ammonia, between two molecules of cuprammine hydroxide with the glucose residue of the cellulose chain, with the hydroxyl groups of the glucose residues being attached to a copper atom (in the anion) and the cuprammonium residue (in the cation), in linkages of the alcoholate type.

2. By our electrophoretic experiments (with and without separation of the electrode spaces) with ammoniacal

solutions of copper hydroxide and cuprammonium solutions of cellulose and its derivatives, alginic acid, Rochelle salt, sugars, and polyhydric alcohols it was shown that, in contrast to the views of Hess and Messmer, copper is formed only at the cathode. Cupricellulose complexes are not displaced toward the anode either in absence or in presence of caustic soda.

3. The hypothesis of the existence of alcoholate copper in cuprammonium cellulose solutions is also not confirmed by our ion exchange experiments. When ammoniacal copper hydroxide solution, and cuprammonium solutions of cellulose, sugars, and hydroxy acids are passed through cationites, ammonia and copper are quantitatively absorbed in every case, while cellulose is deposited on the cationite. When these solutions are passed through an cationites their composition is unchanged, since if copper was present in the anion, copper would be absorbed by the anionite, and the solution would decompose with evolution of cellulose.

4. Cuprammonium cellulose compounds, which do not in reality contain complex anions, should be considered as molecular compounds of variable composition which depends on the equilibrium reactions which take place, and should be likened to alkaline compounds of cellulose (alkali cellulose), which differ from the former only by having a less complicated composition. The solution of polysaccharides in ammoniacal copper hydroxide solutions and in aqueous caustic alkalies has similar features.

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REACTIONS OF DIKETENE

II. REACTIONS OF KETENE WITH INDOLE AND ITS OXYGEN-CONTAINING DERIVATIVES

V. V. Perekalin and N. M. Slavachevskaya

Acetoacetyl derivatives of indole and its oxygen-containing derivatives (indoxyl, oxindole, dioxindole, isatin) are not formed by the action of acetoacetic ester on them.

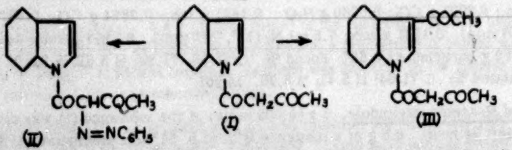
It was therefore of interest to study the reactions of these compounds with diketene in order to obtain a new group of acetoacetic esters — starting materials for the synthesis of various derivatives of the indole series.

The reactive sites in the indole molecule are the secondary amino group and the β-carbon atom, which is activated due to conjugation of the unshared electron pair of the amino groups with the double bond. By analogy with the acetylation of indole [1, 2], its reaction with diketene would be expected to yield N- and C-acetyl derivatives.

Indole in the presence of pyridine [3] formed N-acetoacetylindole (I) by the reaction with diketene. When tertiary amines of different structure but with basicity constants close to that of pyridine were used as catalysts (quinoline, dimethylaniline), the yields of (I) were practically the same; without catalyst the yield of (I) was small, while a highly basic catalyst (triethylamine) directed the reaction toward the formation of dehydroacetic acid, probably as the result of the polymerization rate of diketene being greater than its rate of reaction with indole (see Table 1).

TABLE 1

	Without catalyst	Catalyst			
		Pyridine	Quinoline	Dimethylaniline	Triethylamine
K_b of catalyst	–	$2.4 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$2.7 \cdot 10^{-10}$	$5.6 \cdot 10^{-4}$
Yield of N-acetoacetylindole (I) (in %)	4.4	43.7	45.0	41.0	–



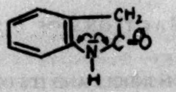
The structure of N-acetylindole (I) was confirmed because: 1) hydrolysis in mild conditions (2% aqueous caustic soda in the cold) resulted in quantitative formation of indole; 2) the azo dye (II) synthesized by coupling (I) with diazobenzene was easily hydrolyzed with the formation of the sodium salt of benzeneazoacetylacetic acid; 3) acylation of (I) by acetic anhydride resulted in the synthesis of N-acetoacetyl-3-acetylindole (III) which was converted by hydrolysis into 3-acetylindole.

If 3-acetoacetylindole had been formed in the given conditions, these reactions could not be carried out.

Indoxyl could form N- and O-derivatives with diketene by reaction with the imino group and transfer of the reaction center to the oxygen atom.

Reaction in benzene solution led to the formation of N-acetoacetylindoxyl (IV) (the O-acyl derivatives are formed by the acylation of indoxyl in an alkaline medium [4, 5] and are hydrolyzed in milder conditions).

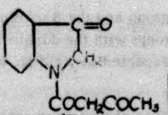
Oxindole, which as a rule reacts in the keto form, did not react with diketene apparently because of reduced basicity of the imino group (conjugation of its unshared electron pair with the carbonyl group).



It was necessary to determine whether the inability of oxindole to react with diketene depends on the simultaneous stabilizing effect of the benzene nucleus and the carbonyl group, or whether the latter plays the decisive role (conjugation with the benzene nucleus alone does not hinder the reaction).

Phthalimidine, in which the imino group is only conjugated with the carbonyl group, gave a quantitative yield of N-acetoacetylphthalimidine (V) with diketene.

In accordance with the above views, dioxindole should not react with diketene. However, it did react, apparently in the dienol form, and yielded a diacetoacetyl derivative. By analogy with the structure of the dibenzene derivative [6] it is probably O,O-diacetoacetyldehydroxyindole (VI).



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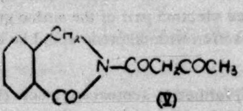
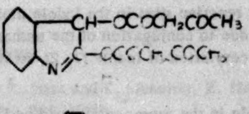


(V)



(VI)

Isatin and phthalimide, like dioxindole, did not react with diketene because of their high acidity (k_a of phthalimide is $5 \cdot 10^{-9}$). It was shown earlier that only substances with k_a of 10^{-10} and less react with diketene [7].

The acylating activity of diketene is lower than that of acetic anhydride; the latter forms acetyl derivatives with oxindole, isatin, and phthalimide.

N-Acetoacetylindole (I). To a solution of 4.86 g (0.04 mole) of indole in a mixture of 20 ml of benzene and 20 ml of toluene at 10°, 0.5 ml of pyridine was added, and then 3.36 g (0.04 mole) of diketene* during 1 hour. The mixture was heated for 1 hour on a boiling water bath. The yellow mass obtained after removal of the excess solvent was treated with 1000 ml of 2% caustic soda solution (in 100 ml portions) until the precipitate was practically all dissolved. After neutralization of the alkaline filtrate with 5% hydrochloric acid solution and a stream of carbon dioxide, a pale pink crystalline precipitate was isolated. M.p. 100° (from ethyl alcohol). N-acetoacetylindole is insoluble in water, ethyl alcohol, or ether; it is readily soluble in benzene, acetone, and chlorobenzene. Yield 3.5 g (43.7%).

0.1115 g sub.: 0.2921 g CO_2; 0.0560 g H_2O. 0.1451 g sub.: 0.3824 g CO_2; 0.0732 g H_2O. 0.1600 g sub.: 9.7 ml N_2 (15°, 767 mm). 0.1241 g sub.: 7.5 ml N_2 (15°, 767 mm). 0.1267 g sub.: 18.02 g benzene: Δt 0.41°. 0.4418 g sub.: 18.02 g benzene: Δt 0.63°. Found %: C 71.50, 71.89; H 5.62, 5.31; N 7.20, 7.18. M 191, 198. $C_{12}H_{11}O_2N$. Calculated %: C 71.64; H 5.47; N 6.96. M 201.

Hydrolysis of N-acetoacetylindole. 1 g (0.005 mole) of the substance (I) was dissolved in 50 ml of 2% caustic soda solution and left 24 hours. 0.5 g of a substance with m.p. 51° was precipitated. No freezing point depression was produced in a sample mixed with indole. Acetone was detected in the filtrate by the formation of indigo with o-nitrobenzaldehyde.

N-Acetoacetylbenzazoindole (II). A solution of 2 g (0.01 mole) of N-acetoacetylindole in 120 ml of ethyl alcohol was mixed with 1 ml of 10% sodium acetate solution. 100 ml (0.01 mole) 0.1 N of diazobenzene was added during 1 hour, with stirring, to the solution cooled to −5°. The solution gradually acquired an intense red color. After 24 hours a yellow precipitate was filtered off and washed with a large volume of alcohol.

The azo dye (II) had m.p. 159-160° (from ethyl alcohol); yield 1.29 g (43%).

0.1411 g sub.: 17 ml N_2 (19°, 763 mm). 0.1213 g sub.: 14.4 ml N_2 (19°, 763 mm). Found %: N 14.01, 13.80. $C_{18}H_{15}O_2N_3$. Calculated %: N 13.77.

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* If the diketene is added without cooling, the yield is rather less, 41%.

Hydrolysis of N-acetoacetylbenzazoindole. 0.3 g (0.001 mole) of the azo dye (II) was heated with 20 ml of 5% caustic soda solution for 3 hours on a boiling water bath. During the heating the color of the precipitate changed from bright yellow to orange. The reaction mass was cooled and filtered. M.p. of the precipitate was 195° (from water).

No freezing point depression was found when a sample was mixed with specially synthesized sodium salt of benzeneazoacetylacetic acid [8]. Yield 0.21 g (91%).

N-Acetoacetyl-3-acetylindole (III). 4 g (0.002 mole) of N-acetoacetylindole and 15 ml of freshly distilled acetic anhydride were heated together for 3 hours at 150-170°. The acetic anhydride was distilled off at 10-15 mm. The transparent brown resinous mass was converted into a white crystalline precipitate after treatment with 25 ml of ethyl alcohol followed by trituration.

N-Acetoacetyl-3-acetylindole, m.p. 178-179° (from ethyl alcohol) is difficultly soluble in most organic solvents. Yield 0.55 g (12.5%).

0.1201 g sub.: 0.3029 g CO_2; 0.0558 g H_2O. 0.1324 g sub.: 0.3363 g CO_2; 0.0648 g H_2O. 0.1423 g sub.: 6.6 ml N_2 (16°, 759 mm). 0.1123 g sub.: 5.4 ml N_2 (19°, 756 mm). 0.3126 g sub.; 7.2 g acetone: Δt 0.32°. 0.2132 g sub.: 7.0 g acetone: Δt 0.25°. Found %: C 68.82, 69.31; H 5.19, 5.47; N 5.43, 5.57. M 226, 203. $C_{14}H_{13}O_3N$. Calculated %: C 69.13; H 5.34; N 5.76. M 243.

Hydrolysis of N-acetoacetyl-3-acetylindole. 0.8 g (0.0032 mole) of the substance (III) was boiled for 1 hour with 10 ml of 5% caustic soda solution. When the solution was cooled, a white flocculent precipitate was formed, which was washed till no alkaline reaction was given.

3-Acetylindole, m.p. 190-191°, sublimed as white leaflets. No freezing point depression was obtained when a sample was mixed with specially prepared 3-acetylindole [2] (m.p. 190-191°).

N-acetoacetylindoxyl (IV). To a suspension of 3.56 g (0.02 mole) of indoxylic acid [9] in 30 ml of benzene, 3 drops of pyridine were added followed by the gradual addition of 3.36 g (0.04 mole) of diketene during 10 minutes. The suspension was then heated 45 minutes on a boiling water bath in a current of hydrogen. After removal of the solvent a brown resin remained, which crystallized on cooling and rubbing. The crystalline mass was treated with 25 ml of ethyl alcohol in the cold, and filtered.

N-Acetoacetylindoxyl, m.p. 110° (from ethyl alcohol), is readily soluble in the cold in acetone, benzene, toluene, and chlorobenzene, and dissolves with difficulty in ether and n-hexane. Yield 0.9 g (37%); when the reaction was carried out without the use of a current of hydrogen, the yield fell to 30%.

0.1196 g sub.: 0.2893 g CO_2; 0.0554 g H_2O. 0.1213 g sub.: 0.2936 g CO_2; 0.0575 g H_2O. 0.1127 g sub.: 6.6 ml N_2 (19°, 775 mm). 0.1273 g sub.: 7.4 ml N_2 (16°, 759 mm). 0.1599 g sub.: 18.46 g benzene: Δt 0.22. 0.2484 g sub.: 18.46 g benzene: Δt 0.32°. Found %: C 66.20, 66.05; H 5.19, 5.31; N 6.74, 6.81. M 206, 214. $C_{12}H_{11}O_3N$. Calculated %: C 66.36; H 5.06; N 6.45. M 217.

Hydrolysis of N-acetoacetylindoxyl. 0.4 g (0.0018 mole) of the substance (IV) was heated for 3 hours with 10 ml of 5% hydrochloric acid at 80-90°; as the heating progressed, a precipitate of indigo was gradually deposited from the solution. 0.19 g of indigo (81%) was isolated. Acetone was detected in the filtrate made alkaline with 10% caustic soda, by the reaction with o-nitrobenzaldehyde.

N-Acetoacetylphthalimidine (V). A solution of 4 g (0.03 mole) of phthalimidine [10] in 40 ml of toluene was mixed with 0.5 ml of pyridine and 5.5 g (0.06 mole) of diketene, heated for 1 hour at 80-85°, and then boiled 10 minutes. When the brown solution was cooled, 6 g of a copious crystalline precipitate was formed; another 0.6 g was isolated from the filtrate.

N-Acetoacetylphthalimidine, m.p. 135-137° (from toluene) is easily soluble in acetone, ether, benzene, and chlorobenzene. Yield 6.3 g (97%).

0.1234 g sub.: 0.3010 g CO_2; 0.0546 g H_2O. 0.1371 g sub.: 0.3323 g CO_2; 0.0634 g H_2O. 0.1465 g sub.: 8.1 ml N_2 (17.5°, 764 mm). 0.1341 g sub.: 7.4 ml N_2 (16°, 770 mm). 0.1339 g sub.; 21.28 g benzene: Δt 0.16°. 0.2393 g sub.: 21.28 g benzene Δt 0.28°. Found %: C 65.56, 66.15; H 4.95, 5.18; N 6.49, 6.55. M 208, 204. $C_{12}H_{11}O_3N$. Calculated %: C 66.35; H 5.07; N 6.45. M 217.

Hydrolysis of N-acetoacetylphthalimidine. A solution of 1 g (0.004 mole) of the substance (V) in 20 g of water was mixed with 0.79 g of soda and boiled for 1 hour. On cooling, 0.6 g of a white crystalline precipitate, m.p. 148-150°, separated out. No freezing point depression was found when a sample was mixed with phthalimidine. Acetone was detected by the o-nitrobenzaldehyde reaction in the alkaline soda filtrate.

2,3-Diacetoacetyldihydroxyindole (VI). 1 g (0.006 mole) of dioxindole [11] was mixed with 30 ml of toluene. 5 drops of pyridine followed by 2 g (0.024 mole) of diketene was added to the suspension. The suspension was heated for 30 minutes with stirring at 50-60°; the dioxindole dissolved.

The brown resin obtained after removal of the solvent, after treatment with 30 ml of cold ethyl alcohol and rubbing, was converted into a white crystalline precipitate of 2,3-diacetoacetyldihydroxyindole; m.p. 170-172° (from ethyl alcohol). The substance is insoluble in most organic solvents. Yield 0.59 g (28%).

0.1481 g sub.: 0.3257 CO_2; 0.0638 g H_2O. 0.1132 g sub.: 0.2510 CO_2; 0.5114 g H_2O. 0.1679 g sub.: 6.3 ml N_2 (19°, 756 mm). 0.1798 g sub.: 7.6 ml N_2 (18°, 757 mm). 0.2046 g sub.; 6.01 g acetone: Δt 0.16°. 0.1600 g sub.: 5.71 g acetone: Δt 0.15°. 0.1521 g sub.; 5.49 g acetone: Δt 0.14°. Found %: C 60.01, 60.51; H 4.95, 5.08; N 4.34, 4.89. M 355, 311, 330. $C_{16}H_{15}O_6N$. Calculated %: C 60.56; H 4.73; N 5.41. M 317.

SUMMARY

1. Acetoacetyl derivatives of indole and its oxygen-containing derivatives are formed by reaction with diketene in presence of basic catalysts.

2. A relationship has been established between the structure of oxygen-containing indole derivatives and their reactivity toward diketene.

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* T. p. = C. B. Translation pagination.

ALKYLATED DIAMINO DERIVATIVES IN THE DIPHENYLETHANE SERIES

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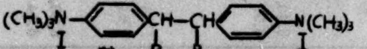
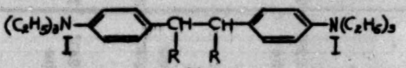
This paper describes the methods of preparation and the properties of diphenylethane derivatives containing either two tertiary, or two quaternary nitrogen atoms, synthesized by the present authors. Such derivatives containing quaternary nitrogen atoms include compounds with curare-like action[1].

The p,p'-diamonium derivatives were prepared by the interaction of the corresponding p,p'-diamino derivatives of diphenylethane with methyl or ethyl iodide. With the use of methyl iodide six p,p'-diammonium derivatives were obtained, with the general formula (I), where R = H, CH_3, C_2H_5, C_3H_7 and C_4H_9 respectively. With R = CH_3, C_3H_7, C_4H_9 only the meso form was obtained, and with R = C_2H_5, both the meso form and the racemate.



(I)

With the use of ethyl iodide two p,p'-diammonium derivatives with the general formula (II) were obtained, where R = CH_3 and C_2H_5 respectively.



(II)

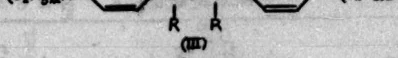
The synthesis of the diamino derivatives used as starting materials was described previously [2].

Good results were not obtained when the methylation and ethylation of diamino derivatives was carried out in the presence of caustic soda. Much better results were obtained when calcium carbonate was used as the substance for binding the acid: the yield was higher and the purification was much simpler.

It was found that the solubility of the above diammonium compouhds in water greatly depends on the nature of the radicals at the nitrogen atoms. Diammonium compounds with methyl groups only at the nitrogen atoms are readily soluble in hot water, while the solubility at room temperature is 0.4-1%. Diammonium compounds with ethyl groups only at the nitrogen atoms are practically insoluble even in hot water.

As was to be expected, the ethylation of the original diamino derivatives was much easier if ethyl iodide was used as the alkylating agent; alkylation proceeded less easily when ethyl bromide was used. By making use of this, we were able as desired to carry the reaction as far as quaternary diammonium derivatives by the use of ethyl iodide, or to tertiary diamines by the use of ethyl bromide.

Thus, with the use of ethyl bromide, three derivatives with two tertiary amino groups, with the general formula (III), were obtained, where R = H, CH_3 and C_2H_5 respectively; in the case of the two latter (when R = CH_3, C_2H_5) the meso form was obtained.



(III)

EXPERIMENTAL

1,2-Diphenylethane-p,p'-bis-(trimethylammonium) iodide. 1.1 g of p,p'-diamino-1,2-diphenylethane (m.p. 137-139°), 1.2g of calcium carbonate, 40 ml of methyl alcohol, 20 ml of water, and 4 ml of methyl iodide were heated together for 6 hours under a reflux condenser on a water bath with the alcohol boiling gently. On the next day 10 ml of water was added, the reaction mixture was boiled for 20 minutes with active charcoal and filtered while hot.

TABLE

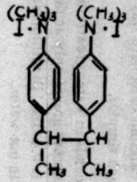
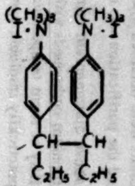
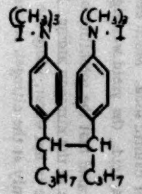
Starting reagents and quantities	Method of purification	Final product		Yield (%)	Found %				Calculated %			
		Structural formula	m.p., color		C	H	N	I	C	H	N	I
1	2	3	4	5	6	7	8	9	10	11	12	13
Meso-p,p'-diamino-2,3-diphenylbutane (m.p. 170-172°) 1.2 g $CaCO_3$ 1.2 g, CH_3OH 40 ml, H_2O 20 ml, CH_3I 4 ml.	Hot filtration. Recrystallization from 40 ml of water		262-265° white	60.4	45.33, 45.45	6.09, 6.41	5.04, 5.12	43.80, 43.68	45.52	5.86	4.86	43.79
Meso-p,p'-diamino-3,4-diphenylhexane (m.p. 140-142°) 8.8 g, $CaCO_3$ 7.8 g, CH_3OH 260 ml, H_2O 120 ml, CH_3I 26 ml.	Filtration. Recrystallization from 100 ml of water. Distillation of methyl alcohol from the aqueous alcoholic liquor. Recrystallization from 60 ml and then 30 ml of water		226-229° white	78	47.14, 47.25	6.40, 6.52	4.88, 4.86	41.66, 41.84	47.37	6.25	4.60	41.77
Meso-p,p'-diamino-4,5-diphenyloctane (m.p. 129-131°) 1 g, $CaCO_3$ 0.8 g, CH_3OH 27 ml, H_2O 14 ml, CH_3I 2.7 ml.	Filtration. Recrystallization from 80 ml of water. Recrystallization of undissolved portion of precipitate from the mother liquor		238-241° white	76.7	49.37, 49.17	6.83, 6.84	4.40, 4.59	40.38, 40.08	49.06	6.60	4.40	40.00

TABLE (continued)

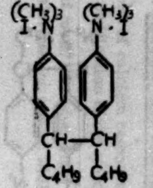
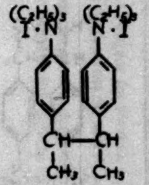
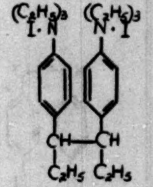
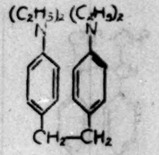
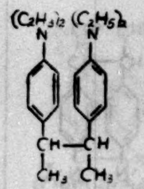
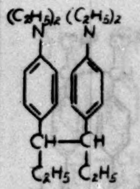
1	2	3	4	5	6	7	8	9	10	11	12	13
Meso-p,p'-diamino-5,6-diphenyldecane (m.p. 105-106°) 1.47 g, $CaCO_3$ 1.2 g, CH_3OH 40 ml, H_2O 20 ml, CH_3I 4 ml.	Cooling in freezing mixture before filtration. Recrystallization from 40 ml of water		218-221° white	73.3	50.24, 50.47	7.11, 7.05	4.52, 4.38	38.17, 38.16	50.60	6.93	4.22	38.25
Meso-p,p'-diamino-2,3-diphenylbutane (m.p. 170-172°) 1.2 g, $CaCO_3$ 1.2 g, C_2H_5OH 45 ml, H_2O 15 ml, C_2H_5I 4.8 ml.	Filtration. Addition of 2.5 ml of 4% hydrochloric acid to the precipitate suspended in 25 ml of water, till an acid reaction to Congo Red		279-282° cream	52	50.28, 50.48	6.97, 7.10	4.50, 4.43		50.60	6.98	4.22	
Meso-p,p'-diamino-3,4-diphenylhexane (m.p. 140-142°) 1.34 g, $CaCO_3$ 1.2 g, C_2H_5OH 42 ml, H_2O 18 ml, C_2H_5I 4.8 ml	Distillation of most of the alcohol under vacuum. Filtration, and treatment of precipitate suspended in water with 4% hydrochloric acid		248-250° pale yellow	58	51.84, 51.76	7.51, 7.30	4.42, 4.22		52.02	7.23	4.05	

TABLE (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
Meso-p,p'-diamino-1,2-diphenylethane (m.p. 137-139°) 1.1 g, $CaCO_3$ 1.2 g C_2H_5OH 35 ml, H_2O 25 ml, C_2H_5Br 2.7 ml.	Filtration. Recrystallization from 40 ml of C_2H_5OH		83-84° white	36.9	81.24, 81.33	9.96, 10.19	8.79, 8.77		81.48	9.86	8.64	
Meso-p,p'-diamino-2,3-diphenylbutane (m.p. 170-172°) 1.2 g, $CaCO_3$ 1.2 g, C_2H_5OH 40 ml, H_2O 25 ml, C_2H_5Br 2.5 ml.	Filtration. Dissolution in 100 ml of hot alcohol and dilution with 37 ml of hot water. Cooling, filtration. Repetition of purification		123-124° white	30.7	81.72, 81.62	10.44, 10.46	8.07, 8.01		81.82	10.33	7.96	
Meso-p,p'-diamino-3,4-diphenylhexane (m.p. 140-142°) 1.34 g, $CaCO_3$ 1.2 g, C_2H_5OH 40 ml, H_2O 25 ml, C_2H_5Br 3 ml.	Filtration. Recrystallization from 80 ml of alcohol		158-159° white	58	81.69, 81.84	10.35, 10.30	7.06, 7.04		82.10	10.50	7.37	

The mixture was cooled and the precipitate formed was filtered off. The weight of the air-dry substance was 2.6 g, m.p. 227-232°. Recrystallization from 30 ml of water with active charcoal yielded 2.17 g of 1,2-diphenylethane-p,p'-bis-(trimethylammonium) iodide, white in color, m.p. 229-232°. Yield 77.5%.

0.1380, 0.1282 g sub.: 0.2204, 0.2034 g CO_2; 0.0652, 0.0638 g H_2O. 0.1583, 0.1526 g sub.: 5.8, 5.6 ml 0.1 N. H_2SO_4. Found %: C 43.55, 43.26; H 5.29, 5.56; N 5.13, 5.14. $C_{20}H_{30}N_2I_2$. Calculated %: C 43.47; H 5.43; N 5.07.

The other diammonium quaternary derivatives, and also the derivatives with tertiary amino groups, were obtained by a method as described above, with some modifications in the methods of isolation and purification of the reaction products. The results of these experiments are shown in the following table.

A description is also given of the preparation of the preparation of 3,4-diphenylhexane-p,p'-bis-(trimethylammonium) iodide racemate, in view of the considerable difference in the method of isolation and purification.

The racemate of 3,4-diphenylhexane-p,p'-bis-(trimethylammonium) iodide. 0.67 g of the racemate of p,p'-diamino-3,4-diphenylhexane (m.p. 70-71°), 0.6 g of calcium carbonate, 20 ml of methyl alcohol, 10 ml of water, and 10 ml of methyl iodide were heated together on the water bath for 5 hours with gentle boiling. On the next day the reaction mixture was filtered to remove a slight precipitate of calcium carbonate and distilled under a vacuum (with the water bath temperature kept not above 60°) to drive off methyl alcohol and water.

15 ml of redistilled acetone was added to the oily residue, and the solution formed was diluted with anesthetic grade ether. The lower layer which separated out was poured into 15 ml of acetone. The solution was left overnight in freezing mixture. The precipitate was filtered off, washed with acetone mixture and dried in a vacuum desiccator. The weight of the precipitate was 1.08 g. The powdered precipitate was thoroughly triturated with 10 ml acetone and filtered off after 2 hours. The yield was 0.8 g of the racemate of 3,4-diphenylhexane-p,p'-bis-(trimethylammonium) iodide, white in color. M.p. 194-196°. Yield 52.6%.

0.2927, 0.2228 g sub.: 10.75 ml (21°, 731.4 mm), 8.5 ml (21°, 736 mm) N_2. Found %: N 4.10, 4.30. $C_{24}H_{38}N_2I_2$. Calculated %: N 4.60.

SUMMARY

1. The alkylation of p,p'-diamino derivatives of 1,2-diphenylethane, meso-2,3-diphenylbutane, 3,4-diphenylhexane (meso and racemate), meso-4,5-diphenyloctane, and meso-5,6-diphenyldecane was studied; a number of new derivatives was produced, both with two quaternary ammonium groups and with two tertiary amino groups.

2. The use of calcium carbonate as the reagent for binding hydrogen iodide favors an increased yield and facilitates the purification of the ammonium derivatives obtained.

3. It was found that when ethyl bromide reacts with p,p'-diamino derivatives, primary amino groups are converted into tertiary amino groups, while when ethyl iodide acts in the same conditions, quaternary ammonium groups are formed.

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* T. p. = C. B. Translation pagination.

ULTRAVIOLET SPECTRA OF SOME NATURAL COUMARINS

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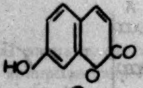
The absorption spectra of natural coumarins, which also include the furocoumarins, have been studied little at the present time. The only information available is on bergaptol [1]; we therefore made a study of compounds belonging to the hydroxy- and methoxycoumarins (umbelliferone, osthole) and also more complex compounds with a furan ring in the molecule (furocoumarins); hydroxypeucedanin, xanthotoxol.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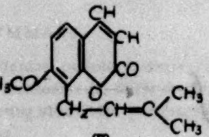
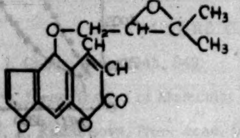
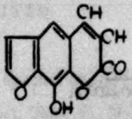

(II)


(III)


(IV)

These compounds are found in the resins of the roots of plants belonging to the Umbelliferae. In particular, osthole, hydroxypeucedanin, and xanthototoxol were found [3, 4] in the roots of Prangos pabularia Lindley, which grow in mountainous and submountainous regions of the Central Asian republics of the USSR. Their simultaneous occurrence in the same plant is rather reminiscent of a similar phenomenon for another class of compounds – the terpenes. Essential oils consisting of terpenes are often found to contain terpenes of closely related structure. A knowledge of the absorption spectra of coumarin derivatives may help in the study of such compounds found in plants. The absorption spectra were studied with the aid of the Q-12 quartz spectrograph. A hydrogen lamp was used as the source of the continuous radiation spectrum. The absorption spectrum of each compound was obtained by two methods; 1) the variable thickness method, which gave a clear qualitative and semiquantitative picture of the molecular absorption spectra, and 2) Henri's method, by which visual photometric measurements could be carried out and the molecular absorption spectra determined. The values obtained were used to plot the molecular absorption curves. The molecular absorption coefficient K was calculated from the Lambert-Beer Formula:

$$K = \frac{\log I \;\; I_0}{cd},$$

where c is the molecular concentration and d is the thickness of the layer.

Absorption spectrum of umbelliferone (hydroxycoumarin) (I). The umbelliferone had m.p. 223-224°. The absorption spectrum was taken in C_2H_5OH solution (0.0251 moles/liter). The absorption curve for umbelliferone (Fig. 1, Curve 1) shows that the absorption region lies in the wave length range 3500-2300 A.

Umbelliferone has one broad band with an absorption maximum at λ 3205 A and one small band with an absorption maximum at λ 2520 A. In comparison with the absorption spectrum of benzene [2] there is a strong shift toward the longer wave lengths, due to structural peculiarities of hydroxycoumarin.

Absorption spectrum of osthole (II). Osthole, isolated from Prangos pabularia resin, with m.p. 84°, was used. The absorption spectrum of osthole was taken in C_2H_5OH solution (0.0241 moles/liter). Figure 1 shows the absorption curve for osthole (Curve 2). The absorption region for osthole lies in the wave length region 3500-2300 A.

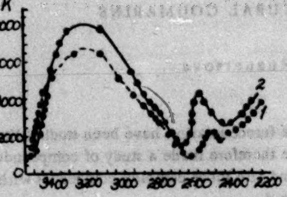


Fig. 1. Absorption curves for umbelliferone (1) and osthole (2).

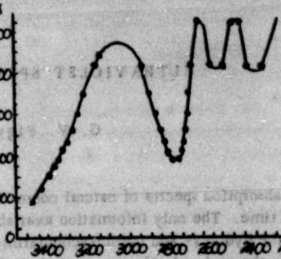


Fig. 2. Absorption curve for hydroxypeucedanin.

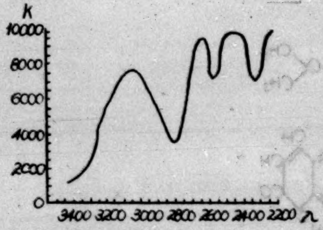


Fig. 3. Absorption curve for xanthotoxol.

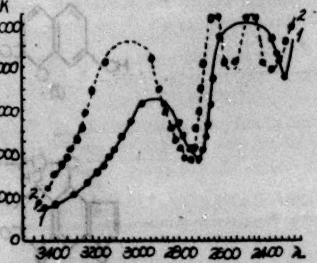


Fig. 4. Absorption curves for substance of m.p. 174-175° (1) and hydroxypeucedanin (2).

The osthole spectrum consists of one broad absorption band with an absorption maximum at λ 3220 A and an absorption band at λ 2585 A. The great resemblance between the spectra of osthole and umbelliferone is explained by the close similarity of their structures.

Absorption spectrum of hydroxypeucedanin (III). Hydroxypeucedanin, like osthole, was isolated from Prangos pabularia resin. M. p. 142-142.5°. The absorption spectrum was taken in C_2H_5OH solution (0.0228 moles/liter). Hydroxypeucedanin (furocoumarin) differs from osthole and umbelliferone by the presence of a furan ring. Absorption in the 2800-2100 A region is characteristic for the latter. The absorption curve for hydroxypeucedanin (Fig. 2) shows that its spectrum, in contrast to the spectra of umbelliferone and osthole, consists of three absorption bands in the wave length range 3500-2200 A. The maxima of the absorption bands are at λ 3060, 2660 and 2495 A. A comparison of the absorption bands of hydroxypeucedanin and osthole shows a difference in their nature, although they both lie in the same wave length region. There is no doubt that structural differences (between coumarin and furocoumarin) determine the features of their absorption spectra.

Absorption spectrum of xanthotoxol (IV). Xanthotoxol was isolated from Prangos pabularia resin. M.p. 243-245° (decomp.). The absorption spectrum was taken in C_2H_5OH solution (0.024 mole/liter). Analysis of the absorption curve of xanthotoxol (Fig. 3) shows that its spectrum consists of three absorption bands in the region 3500-2000 A. The absorption maxima are at λ 3055, 2650 and 2470 A.

The absorption spectrum of the furocoumarin prangenin, described previously [4], is very close to the spectrum of hydroxypeucedanin.

Comparison of the absorption spectra of the three furocoumarins shows great similarity between them: the absorptionbands (see table) of all three substances lie in the same spectral region; the bands have very similar contours, that is, a similar distribution of the absorption intensities in the absorption bands. They are also very similar to the absorption spectrum of bergaptol, described in the literature.

Furocoumarins	Absorption band maxima (A)			Furocoumarins	Absorption band maxima (A)		
Prangenin	3000	2670	2470	Hydroxypeucedanin	3060	2660	2495
Xanthotoxol	3055	2650	2470	Bergaptol	3070	2675	2500

Absorption spectrum of the substance with the composition $C_{15}H_{15}O_4COOH$. The substance of unknown structure was isolated together with the other products from Prangos pabularia resin. Its m.p. was 174-175°. The absorption spectrum was taken in C_2H_5OH solution (0.0251 moles/liter). Fig. 4 shows the absorption curves for the substance with m.p. 174-175° (Curve 1) and hydroxypeucedanin (Curve 2). A comparison of the absorption curves for the two substances reveals some similar features. The absorption bands lie in the same wave length region and have some similarity of outline. There is a difference in the distribution of absorption intensities in the band which lies in the shorter wave region. For example, the maxima of the absorption bands for the substance with m.p. 174-175° lie at λ 2950, 2515 A, and for hydroxypeucedanin at 3060, 2660 and 2495 A. A certain similarity between the spectra of these substances suggests the presence of some common structural elements. The wave length shift in the spectrum of the substance of m.p. 174-175° relative to the spectrum of hydroxypeucedanin may be attributed to the presence of a carboxyl group in the molecule and different positions of the substituents. In addition, according to the formula $C_{16}H_{16}O_6$ ascribed to the substance, it is more saturated than hydroxypeucedanin, $C_{16}H_{14}O_5$, which fully explains the shift of the absorption band into the region of shorter waves.

We express our gratitude to S. N. Andreev for his assistance in the work.

SUMMARY

The spectra of some natural coumarins (umbelliferone, osthole, hydroxypeucedanin, and xanthotoxol) have been obtained for the first time. The absorption spectra of furocoumarins differ sharply from the absorption spectra of hydroxy- and methoxycoumarins. The possibility of using ultraviolet spectroscopy for solving problems of the structure of new compounds of the coumarin series is pointed out.

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* T. p. = C. B. Translation pagination.

REACTIONS OF SYMMETRICAL AROMATIC COMPOUNDS OF MERCURY WITH PHENOLS

I. STUDY OF THE THERMAL STABILITY OF COMPOUNDS OF THE GENERAL FORMULA $(RC_6H_4)_2Hg$

M. M. Koton and V. F. Martynova

One of the present authors [1] earlier developed a method for the mercurization of phenols with the aid of symmetrical aromatic compounds of mercury of the general formula Ar_2Hg. In continuation of this, we studied the reaction between phenols and substituted aromatic bis-compounds of mercury with the general formula $(RC_6H_4)_2Hg$, where R= NH_2, OH, CH_3, NO_2, COOH, in order to investigate the influence of the nature of the substituents on the rate and character of the reaction with different phenols.

The reaction of mercurization by symmetrical mercury compounds proceeds under the influence of heat, and therefore it might be expected, on the basis of the radical mechanism of this reaction, that the ease with which the mercurization reaction proceeds would depend on the thermal stability of the symmetrical mercury compounds; we therefore commenced our research with a study of the thermal stability of symmetrical substituted mercuroorganic compounds of the general formula $(RC_6H_4)_2Hg$. The experiments were carried out at 130-150° for 3 hours, after which the quantity of free metallic mercury evolved was determined.

Our investigations showed that the $(RC_6H_4)_2Hg$ compounds differ in their thermal stability. Mercuroorganic compounds containing substituents of the second type (NO_2, COOH) in the benzene ring were found to be thermally stable, and metallic mercury was not evolved even during heating to 150°.

The mercuroorganic compounds containing substituents of the first type (NH_2, OH, CH_3), on the contrary, already decomposed at 130° with the evolution of metallic mercury, the amount of mercury formed depending on the nature of the substituent in the benzene ring (Table 1).

TABLE 1

Thermal Stability of $(RC_6H_4)_2Hg$ Compounds. Weight taken, 0.2 g; duration of experiment 3 hours

Formula $(RC_6H_4)_2Hg$	Temperature	Amount of metallic mercury formed (in %)	Content of Hg in residue (in %)	
			Found	Calculated
$(p\text{-}H_2NC_6H_4)_2Hg$	130°	23.85	52.09	51.94
$(o\text{-}HOC_6H_4)_2Hg$	130	20.69	51.77	51.53
$(p\text{-}CH_3OC_6H_4)_2Hg$	130	5.05	47.90	48.30
$(m\text{-}NO_2C_6H_4)_2Hg$	150	None	45.20	45.04
$(o\text{-}NO_2C_6H_4)_2Hg$	150	None	44.97	45.04
$(p\text{-}HOOCC_6H_4)_2Hg$	150	None	44.97	44.82

The compounds may be placed in the following series according to their rates of decomposition:

$$(p\text{-}H_2NC_6H_4)_2Hg > (o\text{-}HOC_6H_4)_2Hg > (p\text{-}CH_3OC_6H_4)_2Hg.$$

It only proved possible to draw conclusions concerning the stability of the bonds between mercury and the organic radicals, on the basis of thermal stability studies, for compounds containing substituents of the first type. This was not possible for mercuroorganic compounds containing substituents of the second type in view of their complete thermal stability in such conditions.

It was previously shown [2] that symmetrical aromatic compounds of mercury readily decompose on heating in presence of phenols; the following series was obtained for the decomposition rates of compounds of the formula R_2Hg: $C_6H_5CH_2 > C_6H_5 > C_{10}H_7$.

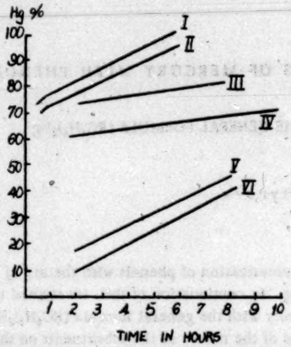
It was therefore decided to use this method to determine the stability of the bond between the mercury atom and the benzene ring containing substituents of the second type. For comparison, these experiments were also performed with mercuroorganic compounds containing substituents of the first type.

The results of the experiments showed that in presence of pyrogallol at 130° the thermal stability of all the $(RC_6H_4)_2Hg$ compounds studied falls sharply, as was shown by the amounts of mercury evolved, which were considerably greater than during ordinary thermal decomposition in absence of pyrogallol (Table 2). In such conditions mercuroorganic compounds with substituents of the second type were also thermally unstable. Their thermal stabilities also differed, and depended not only on the nature of the substituent, but on its position in the benzene ring. Their rates of decomposition form the following series:

$$(m\text{-}O_2NC_6H_4)_2Hg > (o\text{-}O_2NC_6H_4)_2Hg > (p\text{-}HOOCC_6H_4)_2Hg.$$

All the $(RC_6H_4)_2Hg$ compounds studied form the following series according to their decomposition rates in presence of pyrogallol (see figure):

$$(p\text{-}H_2NC_6H_4)_2Hg > (o\text{-}HOC_6H_4)_2Hg > (p\text{-}CH_3OC_6H_4)_2Hg > (m\text{-}O_2NC_6H_4)_2Hg > (o\text{-}O_2NC_6H_4)_2Hg > (p\text{-}HOOCC_6H_4)_2Hg.$$



Decomposition of $(RC_6H_4)_2Hg$ in presence of pyrogallol at 130°.
I) $(p\text{-}H_2NC_6H_4)_2Hg$, II) $(o\text{-}HOC_6H_4)_2Hg$, III) $(p\text{-}CH_2OC_6H_4)_2Hg$, IV) $(m\text{-}O_2NC_6H_4)_2Hg$, V) $(o\text{-}O_2NC_6H_4)_2Hg$, VI) $(p\text{-}HOOCC_6H_4)_2Hg$.

TABLE 2

Thermal Stability of $(RC_6H_4)_2Hg$ Compounds in Presence of Pyrogallol at 130°. Weight taken 0.15 g

Starting substance	Time (hours)	Amount of metallic mercury formed	
		(in g)	(in %)
$(p\text{-}NH_2C_6H_4)_2Hg$	0.5	0.0593	74.55
	1	0.0624	78.15
	2	0.0644	82.20
	3	0.0680	86.85
	4	0.0731	92.15
	5	0.0758	96.80
	6	0.0775	99.82
$(o\text{-}HOC_6H_4)_2Hg$	0.5	0.0505	70.50
	1	0.0529	73.95
	2	0.0566	78.00
	3	0.0600	83.85
	4	0.0624	87.01
	6	0.0690	96.50
$(p\text{-}CH_3OC_6H_4)_2Hg$	2	0.0548	75.45
	4	0.0568	78.15
	6	0.0595	81.80
$(p\text{-}CH_3OC_6H_4)_2Hg$	7	0.0604	83.35
$(m\text{-}NO_2C_6H_4)_2Hg$	2	0.0439	62.64
	4	0.0455	65.94
	6	0.0471	68.21
	8	0.0486	70.20
	10	0.0497	71.69
$(o\text{-}NO_2C_6H_4)_2Hg$	2	0.0130	19.22
	4	0.0183	27.03
	6	0.0250	37.07
	8	0.0319	47.25
$(p\text{-}HOOCC_6H_4)_2Hg$	2	0.0079	11.55
	4	0.0133	21.63
	6	0.0228	31.99
	8	0.0289	42.64

Thermal stability of $(RC_6H_4)_2Hg$ compounds in presence of p-aminophenol and hydroquinone

The thermal stability of $(RC_6H_4)_2Hg$ was studied not only in the presence of pyrogallol, but also in the presence of p-aminophenol and hydroquinone. The results of these experiments were in full qualitative agreement with the results for thermal decomposition, and the difference was purely quantitative. When pyrogallol was replaced by p-aminophenol and hydroquinone, the stability of the $(RC_6H_4)_2Hg$ compounds increased (less mercury was evolved at the same temperature and in the same heating time) (Table 3).

TABLE 3

Comparative Stability of $(RC_6H_4)_2$ in Presence of Additions. Weight taken 0.2 g; duration of experiment 3 hours

Formula of $(RC_6H_4)_2$	Temperature	Evolution of metallic mercury (in %)		
		Pyrogallol	p-Aminophenol	Hydroquinone
$(p\text{-}H_2NC_6H_4)_2Hg$	130°	86.85	74.50	72.38
$(p\text{-}CH_3OC_6H_4)_2Hg$	130	76.43	58.26	52.20
$(m\text{-}O_2NC_6H_4)_2Hg$	150	58.70	10.75	9.50
$(o\text{-}O_2NC_6H_4)_2Hg$	150	30.70	8.79	8.21

EXPERIMENTAL

In all the experiments the substances or mixtures were heated in sealed glass ampoules in an oil thermostat with strict temperature control. In the experiments with pyrogallol, hydroquinone, and p-aminophenol, the contents of the ampoules consisted of a black caked mass containing metallic mercury. The precipitate was treated with an alcoholic solution of 0.5 N caustic potash to remove phenolic oxidation products. The determination of metallic mercury and the analysis for mercury content were carried out by the usual methods.

SUMMARY

1. Substituted diaryl mercury derivatives of the $(RC_6H_4)_2Hg$ type fall into two groups according to their thermal stability – the first, containing substituents of the first type (OH, NH_2, CH_3O), and the second, containing substituents of the second type (NO_2, COOH).

The compounds of the first group are less stable thermally than the compounds of the second group.

2. It is shown that the thermal stability of $(RC_6H_4)_2Hg$ compounds decreases sharply in presence of pyrogallol, p-aminophenol, and hydroquinone, and mercuroorganic compounds with substituents of the second type become unstable in these conditions.

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INVESTIGATION OF THE ACTION OF ALUMINUM CHLORIDE IN A STREAM OF HYDROGEN CHLORIDE GAS ON SOME NAPHTHALENE TETRABROMIDES

Z. I. Stetsura

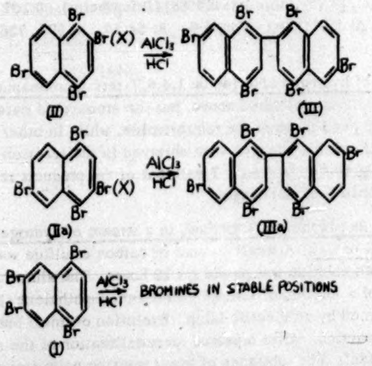
The mobility of the bromine atom in the naphthalene molecule, resulting in its migration from one position to another, has been repeatedly reported in the literature. Roux [1] showed as early as 1887 that α-bromonaphthalene was converted into the β-isomer by gentle heating in carbon disulfide solution in presence of $AlCl_3$. Zalkind and Filinov [2] heated a solution of α-bromonaphthalene in carbon disulfide in presence of $AlCl_3$ and hydrogen chloride, and obtained the β-isomer. Lohfert [3] reported that by the action of $AlCl_3$ in a stream of hydrogen chloride on 1,2-dibromonaphthalene, m.p. 68°, he was able to cause bromine to migrate, in various experiments, from the 1,2 positions to the 1,4, or 1,5, or 2,6 positions.

Lohfert's error was that he incorrectly took the original dibromide to be 1,2-dibromonaphthalene. Actually his dibromide was a mixture of 1,4- and 1,5-dibromonaphthalenes. Lohfert was evidently not aware of the work of Zalkind and Faerman [5], who showed convincingly that direct bromination of naphthalene gives a mixture of 1,4- and 1,5-dibromonaphthalenes, and not the 1,2 isomer. We studied the action of $AlCl_3$ in a current of hydrogen chloride on 1,4-dibromonaphthalene and, in other experiments, on 1,5-dibromonaphthalene, and found that in both cases the bromine atoms migrate to form 2,6-dibromonaphthalene [4].

It was interesting to note the effect of an increase in the number of bromine atoms on their mobility in the naphthalene molecule. We studied 1,4,6,7- (I) and 1,X,4,6-tetrabromonaphthalenes. As was established by Zalkind and Stetsura [6], the latter may have the structure of the 1,2,4,6- (II) or of the 1,3,4,6-isomer (IIa).

Experiments were at first carried out with $AlCl_3$ which was synthesized in the laboratory and sublimed into the reaction vessel. In these conditions the tetrabromides behaved differently. Thus, the tetrabromonaphthalene (I) proved more stable and was isolated unchanged, while the tetrabromonaphthalene in which three bromine atoms are in one ring (II or IIa) condenses to form hexabromonaphthalene,* to which the structure (III or IIIa) may be ascribed (see Scheme 1).

Scheme 1



Quite different results were obtained when the $AlCl_3$ used for the reaction was not sublimed into the reaction vessel, but was in the form of the preparation obtained by Radsiwanowski's method [7], containing an admixture of metallic aluminum. In this case the tetrabromonaphthalene (I) was strongly resinified and a small amount of dinaphthyl (IV) was isolated, while the reaction with the tetrabromonaphthalene (II or IIa) gave hexabromodinaphthyl (III or IIIa) and dinaphthyl (IV) (see Scheme 2).

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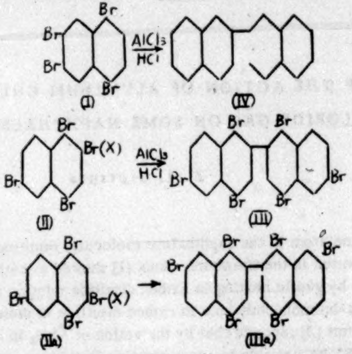
* The following seems to be an error in the original text: "hexabromodinaphthyl" is undoubtedly what is meant here; the schemes do not seem to agree with the text, and Scheme 2 omits the double bonds. – Publisher.

Scheme 2 *



The substitution of bromine atoms by hydrogen in the formation of dinaphthyl apparently took place as the result of a reaction between hydrogen chloride and aluminum. The mechanism of the reaction for the formation of dinaphthyl is as follows: the first step is the condensation of naphthalene tetrabromides to form hexabromodinaphthyl because of the great mobility of bromine in the β-position, then, in presence of active hydrogen, bromine atoms are substituted to form dinaphthyl, while in absence of active hydrogen only hexabromodinaphthyl with m.p. 232° is formed. An increase in the number of bromine atoms in the naphthalene molecule hinders migration and sets up conditions for the reaction to take a new direction. The condensation of naphthalene rings which was observed in our experiments is shown in Schemes 1 and 2.

EXPERIMENTAL

Action of $AlCl_3$ in a stream of hydrogen chloride on 1,2,4,6- (II) or 1,3,4,6- (IIa)tetrabromonaphthalene with m.p. 119-120°. Aluminum chloride was prepared by heating aluminum in the form of granules in a stream of dry hydrogen chloride gas in an electric furnace. The required amount of the prepared $AlCl_3$ was driven off from a retort into the reaction vessel, covered with carbon disulfide, a stream of hydrogen chloride was passed, and a concentrated solution of tetrabromonaphthalene in carbon disulfide was added drop by drop. The reaction mixture was warmed by an electric lamp. The hydrogen chloride gas was passed for 5 hours. The original tetrabromonaphthalene and hexabromodinaphthyl, m.p. 232°, were isolated from the strongly resinified mixture.

0.1112 g sub.: 8.15 ml $AgNO_3$ [T (by bromine) 0.0088] (Pringsheim). 0.132 g sub.; 21 g benzene: Δt 0.045°. 0.0322 g sub.; 0.6044 g camphor: Δt 2.9° (Rost). Found %: Br 64.50. M 699, 736.65. $C_{20}H_8Br_6$. Calculated %: Br 65.96. M 728.

Action of $AlCl_3$ in a stream of hydrogen chloride on 1,4,6,7-tetrabromonaphthalene with m.p. 170-171°. The reaction was carried out in the conditions described above, but the amounts of catalyst were varied. In some experiments 1 mole of catalyst was taken per 1 mole of the tetrabromide, while in other experiments the amount of catalyst was two or three times as much. No visible changes were observed in the reaction mixture during the experiments. Some resin formed on the catalyst grains on heating. Treatment of the products resulted in the original 1,4,6,7-tetrabromonaphthalene being obtained back unchanged.

Action of $AlCl_3$ prepared by Radsiwanowski's method, in a stream of hydrogen chloride on 1,X,4,6-tetrabromonaphthalene with m.p. 119-120° (II or IIa). A small amount of carbon disulfide was poured over 5 g of aluminum grains, and a stream of dry hydrogen chloride was passed for 12 hours. The aluminum granules became coated with a crust of $AlCl_3$. Small portions of a solution of 1,X,4,6-tetrabromonaphthalene (II or IIa) in carbon disulfide were then added. The mixture was warmed by an electric lamp. Evolution of small bubbles of gas, and strong resinification, were observed during the reaction. After repeated recrystallization of the reaction products, two substances were isolated, with m.p. 232 and 185°. The substance of lower melting point was obtained in the form of plates with bluish-pink fluorescence after several recrystallizations from alcohol and acetic acid. This substance did not contain bromine.

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* $AlCl_3$ was prepared by Radsiwanowski's method [7].

0.0766 g sub.; 30.68 g benzene: Δt 0.05°. Found: M 250. $C_{20}H_{14}$. Calculated: M 254.

Analysis of the substance with m.p. 232°.

0.1449 g sub.; 10.5 ml $AgNO_3$ [T (by bromine) 0.0088] (Pringsheim). 0.0548 g sub.; 23.9 g benzene: Δt 0.016°. Found %: Br 63.77. M 718.7. $C_{20}H_8Br_6$. Calculated %: Br 65.96. M 728.

No depression of freezing point was produced when a specimen was mixed with the hexabromodinaphthyl obtained previously.

Action of $AlCl_3$ prepared by Radsiwanoski's method, in a stream of hydrogen chloride on 1,4,6,7-dibromonaphthalene with m.p. 171°. 10 g of 1,4,6,7-tetrabromonaphthalene dissolved in carbon disulfide was added to aluminum chloride prepared by Radsiwanowski's method. Hydrogen chloride was passed for 8 hours. After treatment of the strongly resinified reaction products, a small amount of dinaphthyl with m.p. 185° was isolated. No depression of melting point was obtained when a specimen was mixed with the dinaphthyl prepared previously.

The subject of the present study was proposed by the late Prof. Yu. S. Zalkind.

SUMMARY

1. The mobility of bromine atoms decreases with their increased numbers in the naphthalene molecule.

2. 1,X,4,6-, 1,2,4,6- or 1,3,4,6- tetrabromonaphthalenes give a reaction in which condensation of the naphthalene nuclei takes place, in the same conditions in which bromine migrates from the alpha to the beta position in dibromides.

3. In presence of nascent hydrogen, the condensation of the naphthalene nuclei is preceded by substitution of the bromine atoms by hydrogen.

4. A tetrabromide in which there are three bromine atoms in one ring is more active than a tetrabromide with two bromine atoms in each ring of the naphthalene molecule.

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POLAROGRAPHIC STUDY OF THE HYDROGENATION PROCESS

VI. HYDROGENATION OF MIXTURES OF MESITYL OXIDE WITH DISUBSTITUTED ETHYLENES

A. L. Markman

Skita [1] and Adams [2] have studied the hydrogenation of mesityl oxide, which is a representative of the trisubstituted ethylene group. The behavior of mesityl oxide during hydrogenation of its binary mixtures with disubstituted ethylene derivatives was investigated by S. V. Lebedev [3]. He found that in such mixtures the disubstituted ethylene is hydrogenated first, and mesityl oxide begins to be hydrogenated only after the former is fully saturated.

The polarographic behavior of mesityl oxide [4] was used to study the hydrogenation of some of its binary mixtures with disubstituted ethylene derivatives by the method described previously [5].

EXPERIMENTAL

1. Hydrogenation of a mixture of mesityl oxide with maleic acid in the presence of palladium. 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol for the polarographic analysis. In these conditions mesityl oxide gives no polarographic record, while maleic acid gives a distinct wave (Table 1, Fig. 1). The selectivity index in this case had the value S = 0.988 [6]. In a parallel experiment, S = 0.977.

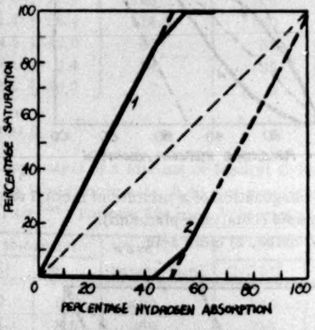

Fig. 1. Hydrogenation of a mixture of mesityl oxide with maleic acid (catalyst – palladium).
1) Maleic acid, 2) mesityl oxide.

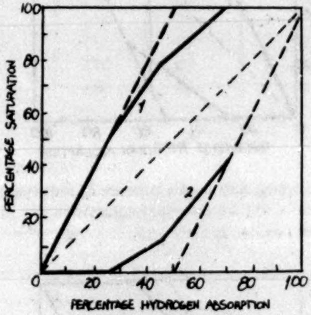

Fig. 2. Hydrogenation of a mixture of mesityl oxide with maleic acid (catalyst – platinum).
1) Maleic acid, 2) mesityl oxide.

TABLE 1

Hydrogenation of a Mixture of Mesityl Oxide with Maleic Acid in the Presence of Pd. 0.58 g of maleic acid, 0.49 g of mesityl oxide; 210 mg of Al, 64 mg of Pd; 30 ml of alcohol and 10 ml of water. Bath temperature 40°, air temperature 16°, Pressure 726 mm. Theoretical absorption of hydrogen H_0 248.2 ml. $\pi_{1/2}$ – 0.73 V

H_2 absorption		Wave height (mm)	Maleic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$*	$\Delta C \cdot 10^{-5}$*	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	440	250	0	0	250	0	0
25.8	10.4	350	198	52	20.8	250	0	0
52.2	21.0	255	145	105	42.0	250	0	0
79.4	32.0	160	90	160	64.0	250	0	0
108.3	43.6	56	32	218	87.2	250	0	0
136.9	55.2	0	0	250	100	225	25	10.0
160.9	64.8	0	0	250	100	176	74	29.6

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* In this and the other tables C is the concentration, and ΔC is the fall in concentration of each of the components. Both values are in moles/liter.

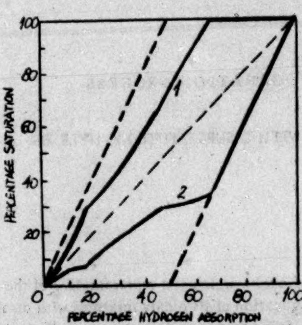

Fig. 3. Hydrogenation of a mixture of mesityl oxide with fumaric acid (catalyst – palladium).
1) Fumaric acid, 2) mesityl oxide.

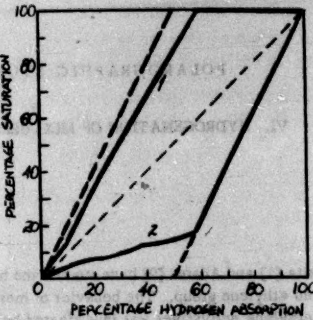

Fig. 4. Hydrogenation of a mixture of mesityl oxide with connamic acid (catalyst – palladium).
1) Cinnamic acid, 2) mesityl oxide.

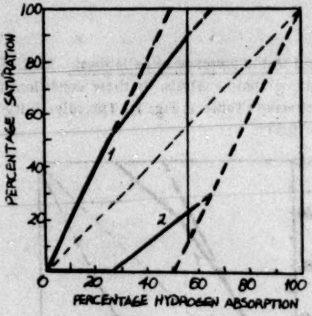

Fig. 5. Hydrogenation of a mixture of mesityl oxide with oleic acid (catalyst – palladium).
1) Mesityl oxide, 2) oleic acid.

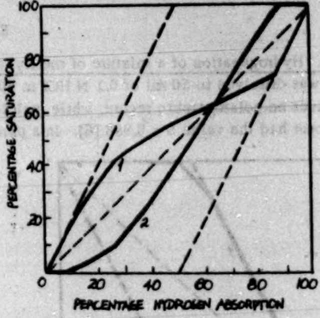

Fig. 6. Hydrogenation of a mixture of mesityl oxide with oleic acid (catalyst – platinum).
1) Mesityl oxide, 2) oleic acid.

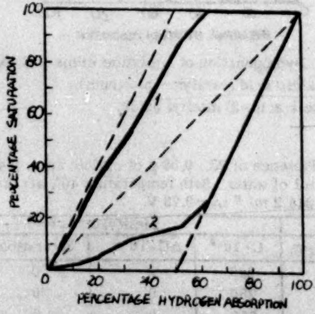

Fig. 7. Hydrogenation of a mixture of mesityl oxide with itaconic acid (catalyst – palladium).
1) Mesityl oxide, 2) itaconic acid.

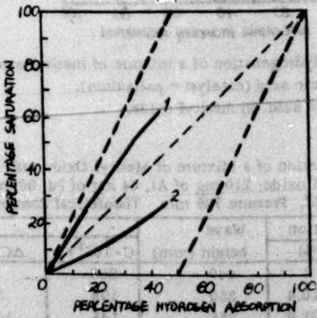

Fig. 8. Hydrogenation of a mixture of mesityl oxide with itaconic acid (catalyst – platinum).
1) Itaconic acid, 2) mesityl oxide.

TABLE 2

Hydrogenation of a Mixture of Mesityl Oxide with Maleic Acid in the Presence of Pt
0.58 g of maleic acid, 0.49 g of mesityl oxide; 210 mg of Al, 116 mg of Pt; 40 ml of alcohol. Bath temperature 40°, air 23°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 256.4 ml

H_2 absorption		Wave height (mm)	Maleic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	775	250	0	0	250	0	0
21.0	8.2	650	209	41	16.4	250	0	0
43.3	16.9	515	166	84	33.6	250	0	0
66.8	26.1	372	120	130	52.0	250	0	0
116.8	45.6	160	52	198	79.2	220	30	12.0
143.5	56.0	92	30	220	88.0	190	60	24.0
172.1	67.1	20	6	244	97.6	158	92	36.8

TABLE 3

Hydrogenation of a Mixture of Mesityl Oxide with Fumaric Acid in the Presence of Pd
0.58 g of fumaric acid, 0.49 g of mesityl oxide, 210 mg of Al, 64 mg of Pd; 40 ml of alcohol. Bath temperature 25°, air 18°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 254 ml $\pi_{1/2} - 0.82$ V

H_2 absorption		Wave height (mm)	Fumaric acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	240	250	0	0	250	0	0
21.1	8.4	2125	221	29	11.6	237	13	5.2
43.3	17.2	176	183	67	26.8	231	19	7.6
66.8	26.5	148	154	96	38.4	214	36	14.4
91.8	36.4	115.5	120	130	52.0	198	52	20.8
118.5	47.0	82	85	165	66.0	180	70	28.0
147.1	58.4	34	35	215	86.0	173	77	30.8
168.6	66.9	0	0	250	100	165	85	34.0

TABLE 4

Hydrogenation of a Mixture of Mesityl Oxide with Cinnamic Acid in the Presence of Pd
0.74 g of cinnamic acid, 0.49 g of mesityl oxide; 210 mg of Al, 64 mg of Pd; 40 ml of alcohol. Bath temperature 25°, air 17°. Pressure 724 mm. Theoretical absorption of hydrogen H_0 249.8 ml $\pi_{1/2} - 1.56$ V

H_2 absorption		Wave height (mm)	Cinnamic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	400	250	0	0	250	0	0
21.1	8.5	350	219	31	12.4	239	11	4.4
43.3	17.3	288	180	70	28.0	233	17	6.8
68.8	27.5	216	135	115	46.0	227	23	9.2
91.8	36.7	155	97	153	61.2	219	31	12.4
118.5	47.4	78	49	201	80.4	214	36	14.4
147.1	58.9	0	0	250	100	205	45	18.0

2. Hydrogenation of a mixture of mesityl oxide with maleic acid in the presence of platinum. The polarographic conditions were the same as in the preceding experiment (Table 2, Fig. 2). S = 0.861.

3. Hydrogenation of a mixture of mesityl oxide with fumaric acid in the presence of palladium. The polarographic conditions were the same as in the preceding experiments (Table 3, Fig. 3). S = 0.621.

4. Hydrogenation of a mixture of mesityl oxide with cinnamic acid in the presence of palladium. 1 ml of each sample was dissolved in 50 ml 0.1 N NH_4Cl in 96% ethanol for the polarographic analysis. In these conditions cinnamic acid gives a wave but mesityl oxide does not (Table 4, Fig. 4). S = 0.802.

TABLE 5

Hydrogenation of a Mixture of Mesityl Oxide with Oleic Acid in the Presence of Pd
1.41 g of oleic acid, 0.49 g of mesityl oxide; 210 mg of Al; 64 mg of Pd, 40 ml of alcohol. Bath temperature 40°, air 22°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 255.5 ml $\pi_{1/2}$ −1.23 V

H_2 absorption		Wave	Mesityl oxide			Oleic acid		
(ml)	(%)	height (mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	95	250	0	0	250	0	0
21.1	8.2	79	209	41	16.4	250	0	0
43.3	17.0	57	165	85	34.0	250	0	0
66.8	26.1	42	119	131	52.4	250	0	0
91.8	35.9	34	90	160	64.0	230	20	8.0
118.5	46.4	22	58	192	76.8	210	40	16.0
143.1	56.0	10	27	223	89.2	193	57	22.8

TABLE 6

Hydrogenation of a Mixture of Mesityl Oxide with Oleic Acid in the Presence of Pt
1.41 g of oleic acid, 0.49 g of mesityl oxide; 210 mg of Al, 116 mg of Pt; 40 ml of alcohol. Bath temperature 40°, air 28°. Pressure 715 mm. Theoretical absorption of hydrogen H_0 262.5 ml

H_2 absorption		Wave	Mesityl oxide			Oleic acid		
(ml)	(%)	height (mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	180	250	0	0	250	0	0
22.7	8.7	150	208	42	16.8	249	1	0.4
46.0	17.5	125	174	76	30.4	238	12	4.8
70.9	27.0	105	146	104	41.6	223	27	10.8
96.4	36.7	90	125	125	50.0	191	59	23.6
123.6	47.1	80	111	139	55.6	154	96	38.4
152.2	58.0	70	97	153	61.2	113	137	54.8
183.0	69.7	59	82	168	67.2	69	181	72.4
216.3	82.4	50	69	181	72.4	19	231	92.4
231.2	88.1	43	60	190	76.0	0	250	100

TABLE 7

Hydrogenation of a Mixture of Mesityl Oxide with Itaconic Acid in the Presence of Pd
0.65 g of itaconic acid, 0.49 g of mesityl oxide; 210 mg of Al, 64 mg of Pd; 40 ml of alcohol. Bath temperature 25°, air 17°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 250.4 ml $\pi_{1/2}$ −0.81 V

H_2 absorption		Wave	Itaconic acid			Mesityl oxide		
(ml)	(%)	height (mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	175	500	0	0	500	0	0
29.5	11.8	170	486	14	2.8	396	104	20.8
52.6	21.0	165	471	29	5.8	319	181	36.2
79.0	31.6	155	443	57	11.4	241	259	51.8
104.0	41.6	150	429	71	14.2	155	345	69.0
130.7	52.3	145	414	86	17.2	63	437	87.4
159.3	63.7	127	363	137	27.4	0	500	100
171.6	68.6	110	314	186	37.2	0	500	100

5. Hydrogenation of a mixture of mesityl oxide with oleic acid in the presence of palladium. 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl in 50% ethanol (Table 5, Fig. 5). S = 0.850.

6. Hydrogenation of a mixture of mesityl oxide with oleic acid in the presence of platinum. The polarographic conditions were the same as in the preceding experiment (Table 6, Fig. 6). During the first half of the process, mesityl oxide is preferentially saturated, with oleic acid being saturated at the same time but more slowly;

near the end of the relative hydrogenation rate of oleic acid increases so much that its saturation is complete before that of mesityl oxide.

TABLE 8

Hydrogenation of a Mixture of Mesityl Oxide with Itaconic Acid in the Presence of Pt
0.65 g of itaconic acid, 0.49 g of mesityl oxide; 210 mg of Al, 116 mg of Pt; 40 ml of alcohol. Bath temperature 27°, air 30°. Pressure 713 mm. Theoretical absorption of hydrogen H_0 265 ml

H_2 absorption		Wave height (mm)	Itaconic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	100	250	0	0	250	0	0
21.1	8.0	87.5	219	31	12.4	241	9	3.6
42.3	16.3	75	188	62	24.8	230	20	8.0
66.8	25.2	62.5	156	94	37.6	218	32	12.8
91.8	34.6	50	125	125	50.0	202	48	19.2
118.5	44.7	37.5	94	156	62.4	182	68	27.2

7. Hydrogenation of a mixture of mesityl oxide with itaconic acid in the presence of palladium. 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 50 % ethanol. Mesityl oxide does not give a wave in these conditions (Table 7, Fig. 7). The selectivity index in this case had the value S = 0.798.

8. Hydrogenation of a mixture of mesityl oxide with itaconic acid in the presence of platinum. 1 ml of each sample was dissolved in 50 ml of the background solution. Otherwise the polarographic conditions were the same as in the preceding experiment (Table 8, Fig. 8).

Thus, in mixtures of mesityl oxide with maleic, fumaric, and cinnamic acids in the presence of palladium, the first to be hydrogenated, in accordance with Lebedev's rule, are disubstituted ethylene derivatives: maleic acid — almost strictly selectively, and the others not so strictly selectively; in mixtures with oleic and itaconic acids, contrarily to Lebedev's rule, mesityl oxide is hydrogenated first. In presence of platinum hydrogenation is also not strictly selective, the disubstituted derivatives being preferentially hydrogenated in mixtures with maleic and itaconic acids; in the mixture with oleic acid, mesityl oxide is hydrogenated more rapidly at first, but later it is overtaken by oleic acid.

SUMMARY

It was established by polarography that mesityl oxide in mixtures with disubstituted ethylenes is either hydrogenated first, contrarily to Lebedev's rule, or second, in accordance with Lebedev's rule, according to the nature of the other component of the mixture and the nature of the catalyst. The selectivity also varies within fairly wide limits according to these factors, and is selective in only one of a number of mixtures studied.

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* T. p. = C. B. Translation pagination.

POLAROGRAPHIC INVESTIGATION OF PAPAVERINE

V. D. Bezuglyi

It is known that papaverine is a substituted derivative of benzylisoquinoline which occurs in opium.

The methods for the quantitative determination of this alkaloid are not numerous and not specific; study of the polarographic determination of this alkaloid is therefore of some interest.

Hamamoto [1] first studied this alkaloid with the aid of the dropping mercury electrode in order to determine the so-called electrochemical adsorption coefficient in KCl solution (10^{-3} N). This was taken as the molar dilution of papaverine at which the maximum on the oxygen reduction curve was halved. Kirkpatrick [2] described catalytic waves for papaverine.

No polarographic waves for papaverine obtained as the result of its direct reduction could be found in the literature.

Method and Results

The work was carried out with the aid of the Giredmet (M-8) polarograph with a galvanometer having the following characteristics: $S = 1.6 \cdot 10^{-9}$ A/mm, t = 6 sec.

The background for the polarographic studies was provided by aqueous and alcoholic solutions of $N(CH_3)_4OH$ of various concentrations.

In the course of the work various capillaries were used: $\underline{\tau}$ from 3 to 8 seconds and $\underline{m}$ from 0.655 to 0.574 mg/seconds. The papaverine was recrystallized from alcohol and water. Its original solution contained 0.0063 mole of papaverine in 1 liter of 96% ethyl alcohol.

Fig. 1 shows the curves obtained on the addition of the alcoholic papaverine solution to 0.01 N solution of $N(CH_3)_4OH$. This figure shows that when papaverine is added to the background solution, a wave with a maximum appears ($E_{1/2} = -1.92$ V relative to the saturated calomel electrode), the height of which at first rises linearly with addition of papaverine (Curves 2 and 3). Upon further addition of papaverine the height of the wave remains practically unchanged, which is apparently due to saturation of the alkaline background solution with papaverine (papaverine is very slightly soluble in alkalies). This is confirmed by the fact that when more alkali is added to the solution the height of the papaverine wave falls sharply (Curve 5) and a white flocculent precipitate of papaverine appears in the solution. In addition, it was noted that increased alkalinity of the background lowers the height of the maximum on the volt-ampere curve for papaverine without altering the value of $E_{1/2}$.

As the applicability of aqueous background solutions of $N(CH_3)_4OH$ is limited because of the poor solubility of papaverine, alcoholic solutions were used, in which papaverine is rather more soluble.

Fig. 2 shows volt-ampere curves given by papaverine in 20% aqueous alcoholic solution of $N(CH_3)_4OH$ (0.02 m); $E_{1/2} = -1.95$. The results obtained were used to plot a calibration graph (Fig. 3).

A characteristic feature of these polarographic curves is the complete absence of the maxima which are so characteristic for the aqueous background solution (Fig. 1) of the same concentration.

Fig. 4 shows polarographic waves for papaverine against a background of 0.02 m. $N(CH_3)_4OH$ in 20, 40, and 90% ethyl alcohol. Distinct waves are obtained for papaverine; they are retained at all the alcohol concentrations studied, and the linear relationship between the wave height and the papaverine concentration is also retained.

The dependence of the wave height on the ethyl alcohol concentration is shown in Fig. 5.

In methyl alcohol the nature of the papaverine waves is changed a little, but the linear relationship between the wave height and the papaverine concentration remains (Fig. 6).

Fig. 7 shows the relationship between E and log $\frac{I}{I_d - I}$ for the papaverine polarographic wave (based on

Fig. 8); Fig. 7 shows that this relationship is represented as a straight line with a slope of 0.115. Thus, the value of *a* is close to 0.5, which indicates irreversible reduction of papaverine.

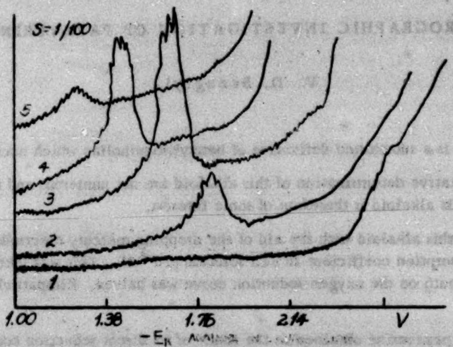


Fig. 1. Polarographic waves for papaverine against a background of $N(CH_3)_4OH$ in water.
1) Background, 10 ml; 2) 0.00022 m; 3) 0.00046 m; 4) 0.00069 m; 5) the last solution with the addition of 0.5 ml of 0.025 N $N(CH_3)_4OH$ solution.

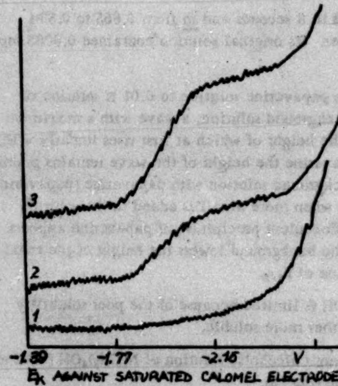


Fig. 2. Polarographic waves for papaverine against background of $N(CH_3)_4OH$ in 20% ethyl alcohol.
1) Background; 2) 0.00023 m; 3) 0.00046 m.

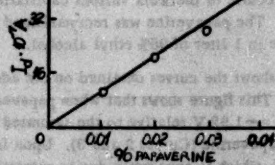
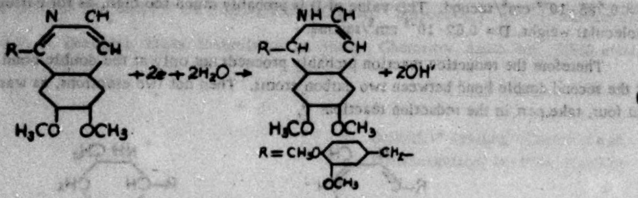


Fig. 3. Calibration graph for papaverine, plotted from the polarographic wave height against background of $N(CH_3)_4OH$ in 20% ethyl alcohol.

Grams taken		Grams found	
Papaverine	Codeine	Papaverine	Codeine
0.0013	0.0018	0.00127	0.00181
0.0011	0.0009	0.00118	0.00094
0.00173	0.0008	0.00163	0.00076
0.0019	–	0.00197	–
0.0004	0.00088	0.00038	0.00087

DISCUSSION

From the structure of the papaverine molecule it may be assumed that its reduction occurs at the double bond between the carbon and nitrogen atoms – the most vulnerable point in the papaverine molecule. As the half-wave potential for papaverine is practically unchanged with change of pH, the reaction of its reduction at the dropping mercury electrode may be represented as follows:



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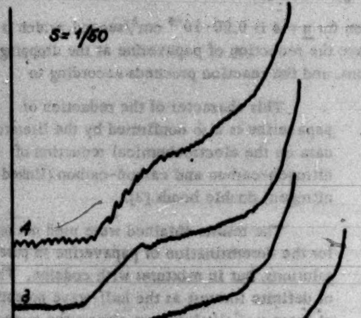


Fig. 4. Polarographic waves for papaverine against a background of 0.02 N $N(CH_3)_4OH$ with various concentrations of ethyl alcohol.
1) In water; 2) in 20% ethyl alcohol; 3) in 40% ethyl alcohol; 4) in 90% ethyl alcohol. Papaverine concentration 0.00096 m.

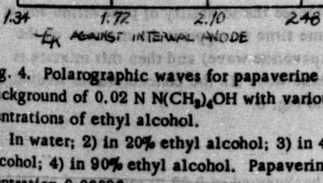


Fig. 5. Variation of the height of the papaverine wave against a background of 0.02 N $N(CH_3)_4OH$ on the concentration of ethyl alcohol.

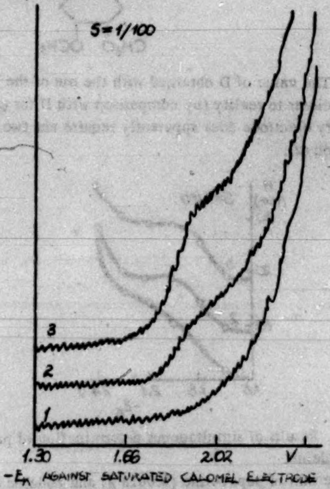


Fig. 6. Polarographic waves for papaverine against a background of 0.02 N $N(CH_3)_4OH$ in 92% methyl alcohol.
1) Background; 2) 0.0117% papaverine solution;
3) 0.0234% papaverine solution.

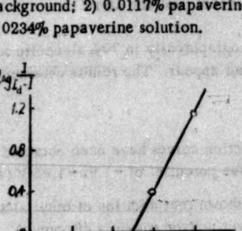
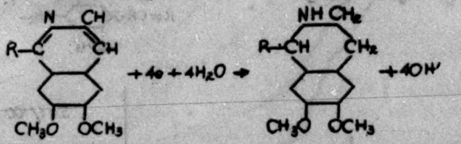


Fig. 7. Relationship between E and log $\frac{I}{I_d - I}$ for the papaverine wave.

The use of the Ilkovich equation to calculate the diffusion coefficient D for papaverine when $\underline{n} = 2$ gives $D = 0.785 \cdot 10^{-5}$ cm^2/second. This value of D is probably much too high, as for caffeine, a substance of much lower molecular weight, $D = 0.62 \cdot 10^{-5}$ cm^2/second.

Therefore the reduction reaction probably proceeds not only at the double bond at the nitrogen atom, but also at the second double bond between two carbon atoms. Then not two electrons, as was assumed in the first instance, but four, take part in the reduction reaction:



(2)

The value of D obtained with the use of the Ilkovich equation for $\underline{n} = 4$ is $0.20 \cdot 10^{-5}$ cm^2/second, which is much closer to reality (by comparison with D for caffeine); therefore the reduction of papaverine at the dropping mercury electrode does apparently require not two but four electrons, and the reaction proceeds according to Equation (2).

This character of the reduction of papaverine is also confirmed by the literature data on the electrochemical reduction of nitrogen-carbon and carbon-carbon (linked to nitrogen) double bonds [3].

The results obtained were used not only for the determination of papaverine in pure solutions, but in mixtures with codeine. This is of definite interest as the half-wave potentials of these two alkaloids are almost the same (for codeine $E_{1/2} = -2.01$ V). However, the different polarographic activities of codeine and papaverine in alcohol [4] make it possible to determine each of these alkaloids separately in a mixture by the polarographic method. For this, the total wave height in 10% alcohol is first determined (an alcoholic solution is used in order to increase the solubility of papaverine and at the same time to suppress the maxima on the papaverine wave) and then this mixture is analyzed polarographically in 70% alcoholic solution, in which the codeine wave (in the concentrations studied, below 0.02 m) does not appear. The results obtained are shown in the table and Fig. 8.

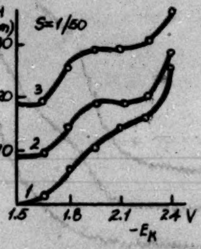


Fig. 8. Results of simultaneous determination of papaverine and codeine.
1) The sum of papaverine (0.0013 g) and codeine (0.0004 g) in 10% ethyl alcohol (volume 15 ml); 2) sum of papaverine (0.0013 g) and codeine (0.0004 g) in 70% ethyl alcohol (codeine wave suppressed); 3) wave for papaverine (0.0013 g) in 70% ethyl alcohol (volume 15 ml).

SUMMARY

1. Reduction curves have been obtained for papaverine against a background of 0.02 m solution of $N(CH_3)_4OH$ with a half-wave potential of −1.92−1.95 V (against the saturated calomel electrode).

2. It is shown that addition of ethyl alcohol to the background solution improves the form of the polarographic wave for papaverine (the maxima disappear).

3. The mechanism of the reduction of papaverine at the dropping mercury electrode was examined and the values of D and $\underline{n}$ determined.

4. The results obtained are shown to be applicable to the quantitative determination of papaverine in mixtures with codeine.

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FORMATION OF DIPHENYLAMINE CARBOXYLIC ACIDS

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It was previously shown that when N-acylated primary aromatic amines are heated with K_2CO_3 under CO_2 pressure, aminocarboxylic acids and derivatives of 2,4-dioxoquinazoline tetrahydride [1].

Peculiar results were obtained when phenyl isocyanate was used as the N-acylamine. This resulted in the formation, in addition to aminocarboxylic acids and 3-phenyl-2,4-dioxoquinazoline tetrahydride, of diphenylamine and diphenylamine carboxylic acids.

The possibility was not excluded that, in the above process, the formation of diphenylamine carboxylic acids is preceded by the formation of the anilide of a diphenylamine N-carbamic acid (for example, from diphenylamine and phenyl isocyanate) which, analogously to the N-acylated primary aromatic amines, is converted into the corresponding carboxylic acids. In this connection the anilide of diphenylamine-N-carbamic acid was prepared. When this was heated in a stream of CO_2 at 220-240°, diphenylamine-4-carboxylic acid was obtained in approximately 20% yield; when the process was carried out at 180-190°, diphenylamine-N-carbamic acid was formed.

The possibility of preparing the corresponding carboxylic acids from the anilides of diphenylamine 3,3'- and 4,4'-dimethyl-N-carbamic acids was investigated. Only traces of the carboxylic acids were obtained, however. Rather better results were obtained with diphenylamine 2-methyl-N-carbamic acid anilide as the starting material.

When diphenylamine N-carbamic acid anilide was heated with K_2CO_3 under CO_2 pressure, diphenylamine-4,4'-dicarboxylic acid was obtained.

As diphenylamine-4,4'-dicarboxylic acid is not described in the literature, it was of interest to synthesize it by another method. Attempts to prepare this acid by condensation of p-bromobenzoic acid or its esters with the potassium salt or the methyl ester of p-aminobenzoic acid in the presence of copper catalysts were not successful.

Diphenylamine-4,4'-dicarboxylic acid was obtained in quite satisfactory yield by oxidation of 4,4'-dimethyl-N-acetodiphenylamine.

In addition, an interesting method for the synthesis of this acid was found by the action of heat on the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid.

EXPERIMENTAL

Experiments on heating phenyl isocyanate with K_2CO_3

100 g of phenyl isocyanate and 140 g of K_2CO_3 were heated in an autoclave of 400 ml capacity at 200-220° for 8 hours. When the reaction mass reached 150-160°, the pressure rose sharply from 1.5 to 16 atm., and at 200° a pressure of 29-30 atm. was established and maintained till the end. At the end of the experiment the reaction mass was treated with 750 ml of water and filtered. The weight of the precipitate (A) was 10.5-11 g. The filtrate was extracted with benzene and acidified till a mineral acid reaction was obtained, to isolate a mixture of diphenylamine carboxylic acids (B). The filtrate from (B) was neutralized to pH 6.5, extracted with ether, and 1.3-1.4 g of aminobenzoic acid was obtained from the ether extract; after recrystallization from water the acid had m.p. 184-186°, and a sample mixed with p-aminobenzoic acid gave no melting point depression. The precipitate (B) was heated in 220 ml of 70% acetic acid, cooled and filtered (this gave filtrate (C), the treatment of which is described below). The undissolved residue (5.4-5.5 g), m.p. 307-311°, was recrystallized from glacial acetic acid in the form of plates, m.p. 322-324°.

3.630 mg sub.: 8.694 mg CO_2; 1.348 mg H_2O. 3.496 mg sub.: 8.389 mg CO_2; 1.380 mg H_2O. 4.443 mg sub.: 0.219 ml N_2 (721.2 mm, 21.4°). 4.980 mg sub.: 0.246 ml N_2 (722.0 mm, 21.0°). Found %: C 65.36, 65.48; H 4.16, 4.42; N 5.42, 5.45. $C_{14}H_{11}O_4N$. Calculated %: C 65.4; H 4.28; N 5.44.

When the product was heated in strong sulfuric acid it did not show the fluorescence characteristic for acridone derivatives, and therefore it did not contain carboxyl groups in the 2 and 2' positions; when heated above its melting point it decomposed with evolution of CO_2 and diphenylamine. A sample mixed with diphenylamine-4,4'-dicarboxylic acid obtained by oxidation of 4,4'-dimethyl-N-acetodiphenylamine melted at 322-324°.

The precipitate (A) was treated with 50 ml of 3% NaOH with warming, cooled, and filtered. The filtrate was acidified till acid to isolate 5.4-5.5 g of a substance which was recrystallized from glacial acetic acid and had m.p. 277-278°. A sample mixed with pure 3-phenyl-2,4-dioxoquinazoline tetrahydride gave no freezing point depression. The substance which did not dissolve in caustic soda (about 4 g) consisted mainly of diphenylamine, which was easily separated by steam distillation (m.p. 53-54°).

The filtrate (C) was diluted with water to give a concentration of 20-25% acetic acid; about 16 g of a resinous substance separated out; when this was washed with water to remove acetic acid, it was converted into a crystalline yellow powder containing diphenylamine p- and o-monocarboxylic acids and certain impurities. To isolate the pure diphenylamine-4-carboxylic acid, the substance was heated to the boil in 80 ml of 25% K_2CO_3 solution, filtered while hot, the precipitate which was deposited from the filtrate was filtered off, washed on the filter with 25% K_2CO_3 solution, treated with dilute hydrochloric acid, filtered again, and washed with water till a neutral reaction was obtained. The result was 5.5-6 g of a substance with m.p. 145-150° which contained diphenylamine-o-carboxylic acid as an impurity, and gave a weak blue fluorescence when heated in concentrated sulfuric acid. To purify the product, it was treated with 40 ml of 14% K_2CO_3 solution and filtered; the filtrate was acidified to isolate 4.5-5 g of a substance which was recrystallized from 50% acetic acid in the form of plates, m.p. 156-157°. The substance gave no fluorescence when heated with concentrated sulfuric acid, and a sample mixed with diphenylamine-4-carboxylic acid (prepared from p-bromobenzoic acid and aniline) of m.p. 157-159°, melted at 157-159°. (The literature gives m.p. 156° for diphenylamine-4-carboxylic acid [2]). The product in sulfuric acid in the presence of nitric acid gave a violet color; when heated above its melting point, it decomposes with evolution of CO_2 and diphenylamine.

Preparation of diphenylamine-4,4'-dicarboxylic acid from 4,4'-dimethyl-N-acetodiphenylamine. 3 g of 4,4'-dimethyl-N-acetodiphenylamine (prepared by heating 4,4'-dimethyldiphenylamine with acetic anhydride, m.p. 84-85°; the literature gives m.p. 85° [3]), 50 ml of water, and 3 g of $KMnO_4$ were heated together to the boil in a flask fitted with a reflux condenser, with stirring. After half an hour's boiling 4 ml of 15% acetic acid was added (to neutralize the alkali) and 3 g of $KMnO_4$, and the mixture was again boiled for 30 minutes, then another 4 ml of 15% acetic acid and another 3 g portion of $KMnO_4$ were added, the mixture boiled for 30 minutes, another 3 ml of 15% acetic acid added, and the mixture kept at the boil for 30 minutes. The mixture was cooled, made alkaline till a definite reaction to Brilliant Yellow was obtained, and filtered. The filtrate was acidified to isolate a viscous product which was dissolved in 60 ml of 6% KOH and boiled for 3 hours. The liquid was then filtered and the filtrate acidified to isolate about 1.9 g of almost pure diphenylamine-4,4'-dicarboxylic acid; after recrystallization from glacial acetic acid this formed plates, m.p. 322-324°. When heated above the melting point the product decomposed with evolution of CO_2 and diphenylamine. The consumption of alkali corresponds to two carboxyl groups. A sample mixed with the dicarboxylic acid prepared from phenyl isocyanate did not show depression of freezing point.

Preparation of diphenylamine-4,4'-dicarboxylic acid from the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid. 8.5 g of the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid (prepared by exact neutralization of diazoaminobenzene-4,4'-dicarboxylic acid by a solution of caustic potash, followed by evaporation to dryness) was heated to 265-270° and held for several minutes at that temperature. The product, yellow at first, became grey at the end of the reaction; it was treated with 70 ml of water and filtered. The filtrate was acidified to isolate about 4 g of a substance, which was heated to 40-50° with 75 ml of water and 10 g of calcium hydroxide, and then filtered. The filtrate was acidified to isolate the dicarboxylic acid with m.p. 315-317°, which was recrystallized from glacial acetic acid to form plates, m.p. 322-324°. The substance corresponded in all its properties to the dicarboxylic acid prepared from phenyl isocyanate; a mixed sample melted at 322-324°.

Experiments on heating the anilide of diphenylamine-N-carbamic acid with K_2CO_3 in the presence of CO_2

Diphenylamine-N-carbamic acid anilide was prepared from diphenylamine and phenyl isocyanate. 127.5 g of diphenylamine was dissolved in 90 g of phenyl isocyanate and left for twenty-four hours; the precipitate was filtered off and washed with alcohol. Crystallization from alcohol gave 113.5 g of a substance with m.p. 136-138°; the mother liquor after recrystallization from toluene gave another 45 g of substance with m.p. 136-138° (136°) [4].

22 g of diphenylamine-N-carbamic acid anilide and 13 g of K_2CO_3 were heated together in a stream of CO_2 in a flask fitted with a stirrer and a reflux condenser (a tube) for 7 hours. In the course of the experiment about 5 g of sublimate collected in the condenser (recrystallization from alcohol gave 4.8 g of diphenylamine with m.p 54°).

The reaction mass (about 25 g) was treated with 150 ml of water at 40-50°, cooled, filtered, and the filtrate acidified to isolate 2.35 g of diphenylamine carboxylic acid, which was mainly the 4-carboxylic acid with a slight impurity of the 2-carboxylic acid. Crystallization from 20% alcohol gave 2.1 g of diphenylamine-4-carboxylic acid, m.p. 155-157°. A sample mixed with pure diphenylamine-4-carboxylic acid gave no melting point depression.

22 g of diphenylamine-N-carbamic acid anilide and 13 g of K_2CO_3 were heated together in a stream of CO_2 for 2 hours at 190-195°, and then 2.5 hours at 240°. About 3 g of a substance was obtained; after recrystallization from 50% acetic acid this formed plates, m.p. 159-160°, a sample mixed with diphenylamine-4-carboxylic acid (m.p. 157-159°) melted at 159-160°. The substance gave a violet color in sulfuric acid in the presence of nitric acid, and when heated above its melting point decomposed with evolution of CO_2 and diphenylamine.

6.580 mg sub.: 17.684 mg CO_2; 2.998 mg H_2O. 6.894 mg sub.: 18.504 mg CO_2; 3.174 mg H_2O. 4.480 mg sub.: 0.271 ml N_2 (724.5 mm, 23°). 4.077 mg sub.: 0.254 ml N_2 (723.1 mm, 24°). Found %: C 73.34, 73.24; H 5.10, 5.15; N 6.65, 6.81. $C_{13}H_{11}O_2N$. Calculated %: C 73.24; H 5.16; N 6.57.

1.4 g of diphenylamine-N-carbamic acid anilide and 1.2 g of K_2CO_3 were heated together at 190° for 2 hours. CO_2 was evolved (absorbed by baryta water). The reaction mass was treated with water, when part of the product dissolved. The liquid was filtered and the filtrate was extracted several times with ether. The clear aqueous solution was acidified, and a precipitate of diphenylamine separated out. It is thus clear that the solution contained a salt of diphenylamine-N-carbamic acid, which was decomposed by acid to give diphenylamine.

27 g of diphenylamine-N-carbamic acid anilide and 15 g of K_2CO_3 were heated together under CO_2 pressure (44-46 atm.) at 240-250° for 4 hours. The reaction mass was treated with 200 ml of water, cooled, and filtered. The filtrate was extracted with ether and the aqueous portion was acidified. About 3.7 g of a substance was obtained, which had m.p. 320-322° after double recrystallization from glacial acetic acid. A sample mixed with pure diphenylamine-4,4'-dicarboxylic acid gave no melting point depression.

SUMMARY

1. It is shown that when phenyl isocyanate and K_2CO_3 are heated together under CO_2 pressure, the products are diphenylamine, diphenylamine-4-carboxylic acid, and diphenylamine-4,4'-dicarboxylic acid.

2. It is shown that when diphenylamine-N-carbamic acid anilide is heated with K_2CO_3 in a stream of CO_2, diphenylamine-4-carboxylic acid is formed, and if the heating takes place under CO_2 pressure, diphenylamine-4,4'-dicarboxylic acid is obtained.

3. It is shown that when the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid is heated, diphenylamine-4,4'-dicarboxylic acid is formed. In view of its simplicity, this method may be of value for preparative purposes.

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• T. p. = C. B. Translation pagination.

5

A CHARACTERISTIC REACTION FOR CYCLOPENTADIENE

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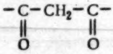
Several qualitative reactions have been proposed for the detection of cyclopentadiene. Vansheidt [1] reported that hydrocarbons containing the $=C-CH_2-C=$ grouping, including cyclopentadiene, when heated in anhydrous acetone or pyridine, give a characteristic color after the addition of one drop of 4 N caustic potash solution in methanol. The color is transient, its shade changes with temperature, and it vanishes when the solution is left to stand in the air.

Terentev and Ivanova [2] proposed two qualitative reactions for the detection of cyclopentadiene in gases. In one of these, cyclopentadiene was evaporated and the vapor was passed in a stream of hydrogen through a solution of mercuric nitrate acidified with nitric acid. It was found that if the gas contained 2% of cyclopentadiene, it was sufficient to pass 2-3 ml of the gas to cause turbidity. However, acetylene gives a similar reaction. Alkenes produce a slight turbidity in the reagent after the gas is passed for 4 minutes, while butadiene has no effect even when passed for 15 minutes through the reagent.

In another reaction, carried out similarly, cyclopentadiene colors a 25% alcoholic solution of benzoquinone intense blue after the addition of several drops of 10% alkali or ammonia solution. However, a similar effect is produced by compounds with labile hydrogen atoms, of the type



$$-\underset{\overset{\|}{O}}{C}-CH_2-\underset{\overset{\|}{O}}{C}-$$

An entirely different color is produced by the action of 2-3 drops of concentrated sulfuric acid on a mixture of acetic acid and chloroform containing a small amount of cyclopentadiene [3]. The test is carried out as follows. A drop of cyclopentadiene is dissolved in a mixture of equal volumes (1 ml each) of acetic acid and chloroform. A reddish-violet color is obtained on the addition of 2-3 drops of concentrated sulfuric acid.

Scagliarini and Lucchi [4], who studied the behavior of cyclopentadiene, indene, propylbenzene, naphthalene, retene, and other cyclic hydrocarbons with alkaline methanol solutions of sodium nitroprusside, reported that cyclopentadiene and indene cause reddening of the nitroprusside solution and formation of a red precipitate.

All these reactions were carried out with pure cyclopentadiene, although it is well known that in industry cyclopentadiene is formed as the result of pyrolysis of petroleum products or high temperature coking of coal, and as a result it is always accompanied by alkenes and various dienes.

In the catalytic production of cyclopentadiene from piperylene at 600° and 10-30 mm, its maximum content in the catalyzate does not exceed 9% [5]. Thus, the condensates contain, in addition to cyclopentadiene, the original piperylene and other unsaturated hydrocarbons.

A critical examination of the reactions proposed for the detection of cyclopentadiene shows that they are not specific. The non-specific nature of some of them is pointed out in the literature. For example, Terentev and Ivanova showed, by the use of piperylene as an example, that the reaction with sulfuric acid in a mixture of acetic acid and chloroform is not specific for cyclopentadiene.

The Vansheidt reagent [1] was really proposed not for cyclopentadiene, but for a group of compounds containing labile hydrogen atoms.

In the description of the reaction with sodium nitroprusside [4] it is pointed out that it is not specific, as indene gives a similar color reaction.

We carefully carried out all these reactions with artificial mixtures of cyclopentadiene with piperylene, pentene-1, diisobutenyl, diisocrotyl, and benzene, and we reached the conclusion that with their aid cyclopentadiene can be identified only in the pure state or in mixtures in which its content is not less than 10%. If considerable amounts of impurities are present (mainly piperylene), none of the proposed reactions reliably detects cyclopentadiene; we therefore attempted to seek a specific reagent by means of which it would be possible to detect cyclopentadiene in mixtures containing not more than 1% of the latter. The following were prepared and tested for their behavior with 90% sulfuric acid containing ferric alum: solutions of 25, 10, and 1% of cyclopentadiene in n-heptane, benzene, piperylene, diisocrotyl, pentene-1, and the pentene mixture obtained by dehydration of isoamyl alcohol.

In addition to the binary mixtures, a ternary mixture was also tested, containing 50% of piperylene, 49% of pentene-1, and 1% of cyclopentadiene.

The tests lead to the conclusion that 90% sulfuric acid containing a small amount of ferric alum is a specific reagent for cyclopentadiene for detecting it in small amounts.

Method of Detection

To prepare the reagent, 100 ml of pure 90% sulfuric acid was saturated with 3 g of finely powdered crystalline ferric alum by periodic shaking for half an hour. After the suspension formed settles, the reagent may be used for the detection of cyclopentadiene. In the solution of ferric alum in sulfuric acid obtained in this way, the iron content is 0.02%.

The qualitative test is carried out by placing 1 ml of the reagent in a test tube, and then adding 1-1.5 ml of the mixture under test down the walls of the tube, so that not less than 0.01 g of cyclopentadiene reacts with the reagent. The test tube is shaken carefully and left to stand about 10 minutes. The reagent becomes almost black with a dark green fluorescent shade by reflected light, and opaque flakes appear on the walls of the tube.

As was to be expected, n-heptane does not react with the reagent, while benzene, pentene-1, and the pentene mixture turn slightly yellow. Piperylene, diisocrotyl, and diisobutenyl give a red color with crimson to cherry-red shades. The results obtained in tests of cyclopentadiene solutions with 25, 10, and 1% contents respectively are shown in the table.

Solvent	Percentage of cyclopentadiene	Color
n-Heptane	25 10 1	Black, with dark green fluorescence
Benzene	25 10 1	Black, with dark green fluorescence
Pentene-1	25 10 1	As with benzene and n-heptane
Mixture of pentenes	25 10 1	As with benzene and n-heptane
Piperylene	25 10 1	As with benzene and n-heptane
50% piperylene and 49% pentene-1	1	Dark brown with fluorescence

As the table shows, 1% cyclopentadiene is reliably detected in all mixtures. The other dienes tested (diisocrotyl, diisobutenyl) give the same color as does piperylene.

If the solvent does not react with the reagent, as n-heptane, cyclopentadiene may be detected in amounts down to 0.1 mg in 1 ml of the solution tested.

If the specific black coloration with a fluorescence is not clearly seen, as may happen when the content of cyclopentadiene in piperylene is close to 1%, water should be added and the test tube shaken in order to ascertain definitely whether the mixture contains cyclopentadiene. After the tube has stood for some time, flakes appear in the aqueous solution, the colors of which depend on the concentration of the cyclopentadiene polymers and their degree of dispersion, while the aqueous layer acquires a pale green color with a violet tinge.

SUMMARY

90% sulfuric acid containing a small amount of ferric alum is a specific sensitive reagent for cyclopentadiene.

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INVESTIGATIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

III. THE PREPARATION OF TRIMETHYL- AND TRIETHYL SILANOLS AND THEIR TRANSFORMATIONS

M. F. Shostakovsky, I. A. Shikhiev, D. A. Kochkin, and V. I. Belyaev

Alkyl or aryl silanols, and in particular trialkyl or triaryl silanols with the general structure R_3SiOH, where R is an alkyl or aryl group, are highly reactive compounds which react with vinyl ethers to give new oxygen-containing organosilicon compounds — organosilicon acetals [1, 2]. The trialkyl or triaryl silanols are intermediates for the preparation of a number of other new compounds. The existing methods for the preparation of the corresponding silanols are still difficult and imperfect, while the properties of these substances are insufficiently well known.

In the present work a study was made of methods for the preparation of trimethyl and triethyl silanols, and also their reactivity with respect to the formation of ethyltrimethyl silane and propyltriethyl silane acetals. This is a continuation of our investigations of oxygen-containing organosilicon compounds [1, 2].

The existence of "silicon hydrates" or silanols was first postulated by D. I. Mendeleev in 1871 in his "Foundations of Chemistry" [3]. Soon after this the first trialkyl silanols were prepared: triethyl silanol [4], tri-n-propyl silanol [5], and triisoamyl silanol [6]. The general method for their preparation was the hydrolysis of the trialkyl halides by caustic soda or ammonia. This method proved unsuitable for the preparation of trimethyl silanol, as it yielded hexamethyl disiloxane instead of the expected trimethyl silanol. The latter was prepared in 1944 from trimethylsilane chloride and gaseous ammonia with the intermediate formation of hexamethyl disilanamine and its subsequent hydrolysis in the presence of mineral acid [7]. In addition, it proved possible to prepare trimethyl silanol by the reaction of methyl polysiloxanes with methylmagnesium bromide or methylmagnesium iodide followed by hydrolysis of the reaction products [7].

It was established as the result of our researches and of a comparative evaluation of the existing methods for the preparation of trialkyl silanols that the most suitable method for the preparation of trimethyl silanol is the ammonolysis of trimethyl silane chloride with the formation of hexamethyl disilanamine followed by its hydrolysis in the presence of mineral acids. The yield of trimethyl silanol was 88.8%.

$$2(CH_3)_3SiCl + 3NH_3 \longrightarrow (CH_3)_3SiNHSi(CH_3)_3 + 2NH_4Cl.$$

$$(CH_3)_3SiNHSi(CH_3)_3 + 2H_2O + HCl + 2(CH_3)_3SiOH + NH_4Cl.$$

Two methods proved most suitable for the preparation of triethyl silanol: 1) hydrolysis of triethyl silane chloride by caustic soda in ether, and 2) reaction between triethyl silane chloride and acetic anhydride followed by hydrolysis of the acetyl derivative. The hydrolysis takes place in milder conditions and does not result in the formation of hexaethyl disiloxane. The preparation of triethyl silanol by this method may be represented by:

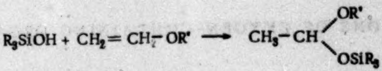
$$(C_2H_5)_3SiCl + (CH_3CO)_2O \longrightarrow (C_2H_5)_3SiOCOCH_3 + CH_3COCl;$$

$$(C_2H_5)_3SiOCOCH_3 + H_2O \longrightarrow (C_2H_5)_3SiOH + CH_3COOH.$$

The triethyl silanol yield was 91%.

Trialkyl and triaryl silanols, and also mixed alkyl aryl silanols, may be considered as derivatives of orthosilicic acid, $Si(OH)_4$, in which three hydroxyl groups are replaced by alkyl or aryl radicals. On the basis of such a structure the properties of the alkyl and aryl silanols would be comparable with those of inorganic acids. However, the replacement of three hydroxyl groups in silicic acid by radicals considerably weakens the properties of the remaining hydroxyl hydrogen, and therefore there is reason to compare the properties of silanols with the properties of the corresponding organic alcohols. The hydroxyl hydrogen of such silanols, as is shown below for a number of reactions, has higher mobility than, for example, in tertiary alcohols.

The reaction between trialkyl silanols, and in particular trimethyl and triethyl silanols, and vinyl ethers is analogous to the corresponding addition reaction of alcohols with formation of mixed acetals of the following structure:



$$R_3SiOH + CH_2{=}CH{-}OR' \longrightarrow CH_3{-}CH\begin{matrix}OR'\\ OSiR_3\end{matrix}$$

where R and R' are the corresponding alkyl or aryl radicals. The reaction takes place even at room temperature in the presence of traces of mineral acids, and is exothermic.

Investigations of combinational light scattering spectra showed that trimethyl silanol is associated in the liquid phase due to hydrogen bond formation. The presence of hydrogen bonding is confirmed by cryoscopic investigations. Trimethyl silanol also forms associated complexes in benzene solution.

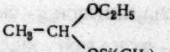
In addition to the high mobility of the hydroxyl hydrogen, trimethyl silanol also has basic properties: it readily splits off water when heated or simply after prolonged standing with formation of hexamethyl disiloxane:

$$2(CH_3)_3SiOH \longrightarrow H_2O + (CH_3)SiOSi(CH_3)_3.$$

The strong association of trimethyl and triethyl silanols in the liquid phase, for example in cyclohexane solution, is also postulated by other authors on the basis of a comparison of the enthalpies and entropies of evaporation [8]. A comparison of the molecular weights of trimethyl and triethyl silanols with those of the corresponding saturated alcohols – trimethyl and triethyl carbinols – established their resemblance. Thus, the association limit of trimethyl silanol is between three and four. The association number of trimethyl carbinol is four, which indicates a special form of association into a four-membered ring. On the other hand, triethyl silanol is much less associated than trimethyl silanol or trimethyl carbinol. The lower association of the more highly alkylated alkyl silanols is explained by greater steric hindrance.

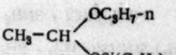
The reactivity of the hydroxyl hydrogen in trialkyl silanols was also demonstrated in the reaction of trimethyl silanol with alkali and sodium [11]. A trimethyl silanolate was formed. Despite the fact that the increased reactivity of trialkyl silanols toward alkalies is reported in the literature, we must point out that this refers mainly to trimethyl silanol. This reaction practically does not occur with other trialkyl silanols, including triethyl silanol. Triethyl silanolate is formed only in the reaction of triethyl silanol with metallic sodium. However, in this instance also, the formation of the triethyl silanolate indicates the reactive nature of the hydroxyl hydrogen in triethyl silanol.

Trimethyl and triethyl silanols were used for the preparation of ethyltrimethyl silane acetal (I) and n-propyltriethyl silane acetal (II):



$$CH_3{-}CH\begin{matrix}OC_2H_5\\ OSi(CH_3)_3\end{matrix}$$

(I)



$$CH_3{-}CH\begin{matrix}OC_3H_7\text{-}n\\ OSi(C_2H_5)_3.\end{matrix}$$

(II)

EXPERIMENTAL

1. Preparation of hexamethyldisilanamine. 109 g of trimethylchlorosilane (b.p. 56-58°) and 500 ml of dry ether were placed in a two-necked flask of 1 liter capacity, fitted with a gas inlet tube and a reflux condenser the upper end of which was connected to a trap immersed in freezing mixture. The reaction flask was placed on a water bath at a temperature of 0- + 7° and a stream of dry ammonia was passed for 9 hours through the solution. The passage of ammonia produced a white precipitate and the mixture became very slightly heated. At the end of the reaction the ether solution was decanted from the ammonium chloride precipitate and filtered. The precipitate was washed several times with dry ether. The ether extracts were combined with the main filtrate and distilled from a Favorsky flask. 52 g of hexamethyldisilanamine (64.2%) was collected after removal of the ether.

B.p. 123-125.6° (757 mm), d_4^{20} 0.7764, n_D^{20} 1.4090, MR_D 51.36; calc. 51.23.

Found %: C 44.71, 44.97; H 11.99, 11.73; Si 35.34, 35.30; N 8.68. M 164. $C_6H_{19}NSi$. Calculated %: C 44.67; H 11.87; Si 34.72; N 8.70. M 161.34.

2. Preparation of trimethyl silanol. 70 g of hexamethyldisilanamine, 50 ml of water, 250 ml of ether, and 10 drops of methyl orange were placed in a three-necked flask fitted with a stirrer with a glycerol seal, a reflux condenser, and a dropping funnel. The reaction flask was placed on a water bath at a temperature of 0-+7°, and 250 ml of N hydrochloric acid solution was added from the dropping funnel. The reaction was completed in 2.5 hours, as was shown by a change in the color of the methyl orange. The ether layer was separated off in a separating funnel and dried with potash. The product was distilled under normal pressure from a Favorsky flask. 69 g (88.8%) of trimethyl silanol was obtained.

B.p. 98-98.6° (757 mm), n_D^{20} 1.3892, d_4^{20} 0.8139, MR_D 26.22; calc. 26.10.

Found %: C 40.78, 40.75; H 11.19, 11.19; Si 30.85, 30.90. M 92.3. $C_3H_{10}OSi$. Calculated %: C 39.96; H 11.16; Si 31.11. M 90.17.

3. Preparation of triethyl silanol. a) 151.0 g of triethylchlorosilane (b.p. 143.0-144.0° at 753 mm, n_D^{20} 1.4310, d_4^{20} 0.8970) and 102.1 g of anhydrous acetic anhydride (b.p. 140°, n_D^{20} 1.3900, d_4^{20} 1.0800) were placed in a two-necked flask 0.5 liter in capacity, fitted with a thermometer and a reflux condenser with an outlet tube and a thermometer in its upper part. The reaction mixture was heated on an oil bath at the boiling point for 5-6 hours. The acetyl chloride formed in the reaction was driven off through the outlet tube of the condenser. The boiling under reflux was stopped after all the acetyl chloride was driven off, which was determined from the amount of it in a graduated receiver and the increase in the vapor temperature of the reaction mixture. The residue in the flask after removal of the acetyl chloride was introduced dropwise from a dropping funnel under a layer of aqueous ammonia with constant stirring (500 ml of water and 20 ml of 18% ammonia). The temperature of the reaction mixture did not exceed +6°. The triethyl silanol formed floated as an oily layer. This was separated from the aqueous layer, washed with two portions of water, dried over potash, and fractionated from a Favorsky flask. This gave 99.2 g (75%) of triethyl silanol.

B.p. 80° (30 mm), 153.5-154.5° (753 mm), n_D^{20} 1.4341, d_4^{20} 0.8646.

Found %: C 54.32, 54.45; H 12.13, 12.17; Si 21.20, 21.25. $C_6H_{16}OSi$. Calculated %: C 54.50; H 12.19; Si 21.22.

b) 100.0 g of triethylchlorosilane (b.p. 143.0-144.0° at 753 mm, d_4^{20} 0.9220), 500 ml of anhydrous ether, and several drops of phenolphthalein were placed in a three-necked flask 1.0 liter capacity, fitted with a mechanical stirrer and a dropping funnel. The reaction mixture was cooled to −5° and N NaOH solution was added with vigorous stirring until a permanent pale pink color was produced. The temperature of the reaction mixture did not exceed +2°. The ether layer was then separated from the aqueous layer and dried with potash. After removal of the ether the reaction mixture was fractionated under vacuum and the fraction with b.p. 76-80° (30 mm) was isolated. A second fractionation yielded 68.8 g (91%) of a substance with the following constants:

B.p. 80° (30 mm), n_D^{20} 1.4340, d_4^{20} 0.8645, MR_D 39.85; calc. 40.08.

Triethyl silanol is a mobile colorless liquid with a camphor-like smell, partially soluble in water, easily soluble in organic solvents. It can be kept for a long time in a glass flask with a ground glass stopper. Strong heating in the presence of mineral acids converts it into hexaethyl disiloxane. It does not react with solutions of alkalies. It reacts vigorously with metallic sodium or potassium on heating.

4. Synthesis of ethyltrimethylsilane acetal. (Jointly with V. M. Vlasov). An ampoule cooled to −8° was filled with 22.5 g of trimethyl silanol (b.p. 98.0-99.0°, n_D^{20} 1.3892, d_4^{20} 0.8139), 21 g of vinyl ethyl ether (b.p. 36.0-37.0°, n_D^{20} 1.3776, d_4^{20} 0.7730) and 0.004 g of concentrated hydrochloric acid. The sealed ampoule was heated in a thermostat at 65° for 8 hours. After treatment of the reaction product with calcined potash and distillation from a Favorsky flask fitted with a trap cooled by ice and salt, the following fractions were isolated: 1st to 21° (17 mm), 23.4 g, n_D^{20} 1.3825; 2nd 37-38° (17 mm), 6.8 g, n_D^{20} 1.3937; residue 2.3 g. The 8.3 g of the product collected in the trap was added to the 1st fraction and treated with metallic sodium. Distillation of the 1st fraction under atmospheric pressure gave 18.4 g of a product with b.p. 99-100°, n_D^{20} 1.3784, d_4^{20} 0.7632, and 5.4 g of a product with b.p. 102-104°, n_D^{20} 1.3806, d_4^{20} 0.8236. These data indicate that the product with b.p. 99-100° is hexamethyl disiloxane, and the product with b.p. 102-104° is the symmetrical diethyl acetal *.

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* Literature data for hexamethyl disiloxane: b.p. 98.5° (740-760 mm), n_D^{25} 1.3730, d_4^{25} 0.756 [9]; for the symmetrical diethyl acetal: b.p. 103-104°, n_D^{20} 1.3820, d_4^{20} 0.8254 [10].

A second fractionation of the 2nd fraction with b.p. 37-38° (17 mm) yielded 6.2 g of a product with the following constants:

B.p. 38-39° (16-17 mm), n_D^{20} 1.3940, d_4^{20} 0.8346, MR_D 46.43; calc. 46.70.

Found %: C 51.90, 52.01; H 11.37, 11.47; Si 16.80, 17.80. M 154.5, 158.2. $C_7H_{18}O_2Si$. Calculated %: C 51.79; H 11.18; Si 17.29. M 162.2.

These results correspond to ethyltrimethylsilane acetal; the yield was 15.3% on the original trimethyl silanol. The product is a transparent liquid with a faint ethereal smell; it is insoluble in water, and readily soluble in alcohol, acetone, ether, and chlorinated hydrocarbons.

5. Synthesis of n-propyltriethylsilane acetal. A wide necked ampoule was filled with 33 ml of triethyl dilanol (b.p. 80° at 30 mm, n_D^{20} 1.4332, d_4^{20} 0.8645) and 21.5 g of vinyl n-propyl ether (b.p. 65.0-65.3°, n_D^{20} 1.3920, d_4^{20} 0.7678). 0.02 ml of 30% hydrochloric acid was added to the mixture. The temperature of the contents of the ampoule gradually rose to 40° on shaking. The ampoule was then sealed and heated in a thermostat at 65° for 10 hours. On the following day the ampoule was opened, the contents dried over potash, and distilled under vacuum; this yielded 46 g of a fraction with b.p. 91-92° (14 mm), n_D^{20} 1.4254. A second distillation gave 35 g of a product with the following constants:

B. p. 89-90° (13-14 mm), 204-205° (760 mm), n_D^{20} 1.4250, d_4^{20} 0.8572, MR_D 65.03; calc. 65.22.

Found %: C 60.21, 60.10; H 12.13, 11.95; Si 13.50, 13.88. $C_{11}H_{26}O_2Si$. Calculated %: C 60.49; H 12.00; Si 12.84.

This substance was n-propyltriethylsilane acetal, the yield being 67.45% calculated on the triethyl silanol taken. It is a colorless liquid with an ethereal odor, soluble in alcohol, ether, acetone, chlorinated and aromatic hydrocarbons, insoluble in water.

SUMMARY

1. Methods for the preparation of trimethyl and triethyl silanols in good yields have been modified and improved.

2. The following organosilicon acetals have been obtained for the first time: ethyltrimethylsilane acetal, by the reaction of vinyl ethyl ether with trimethyl silanol, and n-propyltriethylsilane acetal, by the reaction of vinyl propyl ether with triethyl silanol.

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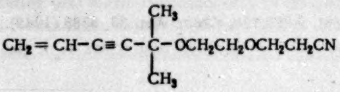
CONDENSATION OF DIMETHYLVINYLETHYNYL CARBINOL WITH ETHYLENE OXIDE

E. S. Lagucheva

As was reported previously [1, 2], when dimethylethynyl carbinol is heated in an autoclave with alkylene oxides in the presence of tertiary organic compounds, the corresponding β-hydroxyalkyl ethers are formed in good yields. It was desired to verify the applicability of this method to the preparation of the β-hydroxyethyl ether of dimethylvinylethynyl carbinol, especially because this compound is obtained in low yields by the previously described methods [3, 4] for its synthesis.

When the condensation of dimethylvinylethynyl carbinol with ethylene oxide was carried out in the presence of dimethylaniline, the β-hydroxyethyl ether of dimethylvinylethynyl carbinol was obtained. The use of dimethylaniline as a catalyst, which also acted as a polymerization stabilizer, proved very successful in completely preventing resin formation.

The β-hydroxyethyl ether of dimethylvinylethynyl carbinol was identified by conversion into the β-cyanoethoxyethyl ether of dimethylvinylethynyl carbinol •.



$$CH_2{=}CH{-}C{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCH_2CH_2OCH_2CH_2CN$$

EXPERIMENTAL

β-Hydroxyethyl ether of dimethylvinylethynyl carbinol. 330 g (3 moles) of the freshly distilled carbinol, 44 g (1 mole) of ethylene oxide, and 11.6 g (3.5% on the carbinol) of dimethylaniline were placed in an autoclave fitted with a manometer. The autoclave was placed in an oil bath, and the reaction was continued for 7 hours at a bath temperature of 60-85°; no increase of pressure was observed. At the end of the process the excess carbinol (252 g) was removed from the reaction mixture under vacuum with the aid of a fractionating column. The residue was fractionated under vacuum from a Claisen flask; the following main fractions were obtained: 1st, b.p. 80-82° (4 mm), 75.5 g; 2nd, b.p. 114-116° (4 mm), 7 g.

The first fraction, obtained in 69.2% yield, had the following data:

d_{20}^{20} 0.9515, n_D^{20} 1.4797 (n_D^{15} 1.4819), MR_D 45.9; calc. 44.46.

Found %: OH 10.46, 10.67 (phthalation). $C_9H_{14}O_2$. Calculated %: OH 11.03.

By its boiling range and refractive index this fraction corresponded to the β-hydroxyethyl ether of dimethylvinylethynyl carbinol, for which the literature gives: b.p. 80-81° at 4 mm, n_D^{15} 1.4811 [4], n_D^{17} 1.4820 [3].

The 2nd fraction, b.p. 114-116° at 4 mm, corresponded to the glycol ether of dimethylvinylethynyl carbinol (yield 6.4%), for which the literature gives; b.p. 103-104° at 2 mm, n_D^{15} 1.4811.

β-Cyanoethoxyethyl ether of dimethylvinylethynyl carbinol. 31 g (0.2 mole) of the β-hydroxyethyl ether of dimethylvinylethynyl carbinol was mixed with 1.86 g of 40% aqueous caustic soda solution, and 12 g (0.22 mole) of acrylonitrile was then added to the solution heated to 30°. The process was continued 4 hours at 30-35°. At the end of the reaction the product was separated from the aqueous layer, neutralized with dilute hydrochloric acid, and fractionated under vacuum. 4 g of the original β-hydroxyethyl ether of dimethylvinylethynyl carbinol was driven off. The β-cyanoethoxyethyl ether of dimethylvinylethynyl carbinol was collected in the range 129-131° at 3 mm. It was a pale, mobile, easily polymerized liquid. The yield was 21 g of the β-cyanoethoxyethyl ether of

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• In our paper on the cyanoethylation of acetylenic alcohols [5], the source [6] in which the cyanoethylation of dimethylethynyl carbinol was described, was omitted.

dimethylvinylethynyl carbinol, which was 60% calculated on the β-hydroxyethyl ether of dimethylvinylethynyl carbinol which entered the reaction.

d_{20}^{20} 0.9709, n_D^{20} 1.4636, MR_D 58.80; calc. 57.97.

0.2672 g sub.: 13.68 ml 0.1 N H_2SO_4 0.3297 g sub.: 16.46 ml 0.1 N H_2SO_4. Found %: N 7.17, 6.99. $C_{12}H_{17}O_2N$. Calculated %: N 6.76.

SUMMARY

1. It is shown that when dimethylvinylethynyl carbinol is heated with ethylene oxide in an autoclave in the presence of dimethylaniline, the β-hydroxyethyl ether of dimethylvinylethynyl carbinol is formed in good yield.

2. The synthesis of the β-cyanoethoxyethyl ether of dimethylvinylethynyl carbinol is described.

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STUDY OF TAUTOMERIC COMPOUNDS

XVII. THE REACTION OF DIAZO COMPOUNDS WITH CONDENSATION PRODUCTS OF PHENYLMETHYLPYRAZOLONE AND KETONES

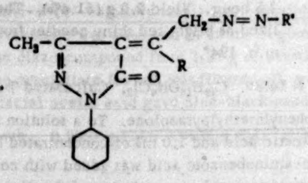
A. E. Poraj-Koshits* and M. S. Dinaburg

As was already reported, the condensation products of phenylmethylpyrazolone and methyl ketones are distinguished by the high mobility of the hydrogen atoms in the methyl groups [1]. Somewhat earlier one of the present authors [2] showed by a number of examples that in the presence of higher hydrogen atom activity in the methyl groups the compounds are capable of entering coupling reactions with diazo compounds.

Such compounds include mesomethylacridine [3], isopropylidene and phenylethylidene derivatives of isooxazolones [4], trinitrotoluene [5] and some others [6]. Instances are known when the power to enter this reaction appears only after additional activation of the hydrogen atoms. Kōnig [7] was the first to point out that lepidine and quinaldine derivatives are capable of reacting with diazo compounds only in the form of anhydro-bases of the haloalkyl derivatives. Simple salt formation is sometimes sufficient for this. Indeed, the coupling reaction of mesomethylacridine takes place successfully only in an acetic acid medium, when the mesomethylacridine is present in the form of an oxonium salt [8].

Our investigations showed that phenylmethylpyrazolone derivatives, containing a methyl ketone residue, are also capable of coupling with diazo compounds. The reaction may only be brought about in a mineral acid medium, and apparently the previous formation of an onium salt (through the imino nitrogen of the pyrazolone ring) is just as essential as in the coupling of mesomethylacridine. However, because of the very low basicity of these derivatives they can only form salts with strong mineral acids [9].

In such conditions the reaction with diazo compounds occurs with practically all available diazo compounds and results in the formation of deeply colored compounds, to which we assign the following structure on the basis of their properties and analytical data:



where R' = aryl, and R = CH_3, C_6H_5 or m-$NO_2C_6H_4$

The absorption spectra of the compounds formed show considerable intensification of color in comparison with phenylmethylpyrazolone derivatives which do not contain intermediate ketone residues, and, as in the case of condensation products with aldehydes, the presence of two maxima. The position of one of these, in the visible part of the spectrum, is determined by the nature of the side chain; the second maximum, in the ultraviolet region of the spectrum at λ = 250 mμ is constant for all the phenylmethylpyrazolone derivatives, and its formation is evidently due to the action of the pyrazolone ring.

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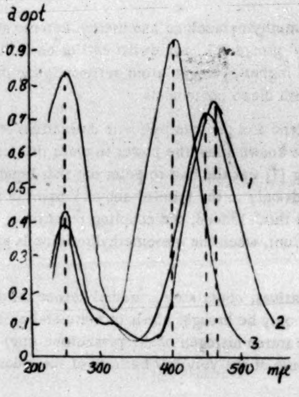
* Deceased:

EXPERIMENTAL

Coupling of 4-isopropylidenephenylmethylpyrazolone with diazo compounds

4-[α-Methyl-β-(phenylazo)]-ethylidenephenylmethylpyrazolone. 0.93 g of aniline in 2 ml of concentrated hydrochloric acid and 1-2 ml of water was diazotized at 0° with 0.7 g of nitrite in 2 ml of water. Urea was added to the diazonium salt solution to remove excess nitrous acid. The diazonium solution was added dropwise at 0° to 2.14 g of isopropylidenephenylmethylpyrazolone in 25 ml of glacial acetic acid and 0.7 ml of concentrated hydrochloric acid. A crystalline precipitate was formed immediately; this was filtered off after 1-1.5 hours, washed with alcohol and dried. Yield 1.8 g (56.6%). The substance formed bright red scales from glacial acetic acid. M.p. 173-174°.

0.1476 g sub.: 22.5 ml N_2 (17°, 755 mm). 0.1077 g sub.: 16.4 ml N_2 (17°, 756 mm). 0.1067 g sub.: 0.2794 g CO_2; 0.0526 g H_2O. Found %: C 71.40; H 5.46; N 17.85, 17.76. $C_{19}H_{18}ON_4$. Calculated %: C 71.69; H 5.66; N 17.61.



1) 4-[α-phenyl-β-(phenylazo)ethylidene]-1-phenyl-3-methylpyrazolone-5; 2) 4-[α-methyl-β-(phenylazo)-ethylidene]-1-phenyl-3-methylpyrazolone-5; 3) 4-phenylazo-1-phenyl-3-methylpyrazolone-5.

4-[α-Methyl-β-(4'-nitrophenyl)-azo]-ethylidenephenylmethylpyrazolone. This was obtained in a manner analogous to the above from 2.14 g of isopropylidenephenylmethylpyrazolone in 50 ml of glacial acetic acid and diazotized p-nitroaniline. Yield 2.76 g (76%). Crystallization from a large amount of glacial acetic acid gave fine reddish-violet needles, m.p. 234-236°.

0.1437 g sub.: 0.3296 g CO_2; 0.0657 g H_2O. Found %: C 62.57; H 4.50. $C_{19}H_{17}O_3N_5$. Calculated %: C 62.80; H 4.68.

4-[α-Methyl-β-(2',5'-dichlorophenyl)-azo]-ethylidenephenylmethylpyrazolone. 2.14 g of isopropylidinephenylmethylpyrazolone was dissolved in 50 ml of glacial acetic acid and 1.0 ml of hydrochloric acid (d = 1.19). A solution of freshly prepared zinc chloride diazonium double salt, obtained from 1.62 g of dichloroaniline, in 15 ml of water, was added to the thoroughly cooled solution with stirring. Separation of a crystalline precipitate commenced immediately. The precipitate was filtered off after 2.5 hours. Yield 2.0 g (51.4%). The substance crystallized as bright red shiny needles from acetic acid, m.p. 194°.

0.1133 g sub.: 14.2 ml N_2 (18°, 767 mm). Found %: N 14.80. $C_{19}H_{16}ON_4Cl_2$. Calculated %: N 14.47.

4-[α-Methyl-β-(3'-carboxyphenyl)-azo]-ethylidenephenylmethylpyrazolone. To a solution of 2.14 g of isopropylidenephenylmethylpyrazolone in 25 ml of glacial acetic acid and 1.0 ml of concentrated hydrochloric acid a solution of the diazo compound obtained from 1.37 g of m-aminobenzoic acid was added with cooling and stirring. The reaction is rather slow, and the addition was regulated so as to avoid accumulation of the diazo compound in the solution. A copious crystalline precipitate began to form 30 minutes after all the diazo solution had been added. Yield 1.74 g (49.1%). Crystallization from a large amount of acetic acid gave violet-red crystals, m.p. 235-236°. Careful dilution of the mother liquor with 30 ml of water yielded a further 0.5-0.6 g of the substance. The total yield was 227 g (62%).

0.1734 g sub.: 0.4209 g CO_2; 0.0804 g H_2O. Found %: C 66.21; H 5.14. $C_{20}H_{18}O_3N_4$. Calculated %: C 66.29; H 4.97.

4-[α-Phenyl-β-(2',5'-dichlorophenyl)-azo]-ethylidenephenylmethylpyrazolone. 2.76 g of 4-α-phenylethylidenephenylmethylpyrazolone in 25 ml of glacial acetic acid was mixed with a solution of the zinc chloride double salt of the diazonium compound prepared from 1.6 g of 2,5-dichloroaniline, in 10 ml of water. 0.5 ml of hydrochloric acid (d = 1.19) was added dropwise to the pale yellow solution of the two components. Each drop of acid left a brightly colored trace in the solution, and crystallization commenced at once. After a few minutes the precipitate was filtered off, washed with alcohol, and dried. Yield 4.0 g (87%). Crystallization from a large amount of alcohol gave violet-red leaflets or violet-brown needles, m.p. 185-186°.

0.1279 g sub.: 13.5 ml N_2 (18°, 764 mm). 0.1359 g sub.: 14.3 ml N_2 (18°, 768 mm). 0.1779 g sub.: 0.1080 g AgCl. Found %: N 12.42, 12.50; Cl 15.46. $C_{24}H_{18}ON_4Cl_2$. Calculated %: N 12.47; Cl 15.80.

4-[α-Phenyl-β-(4'nitrophenyl)-azo]-ethylidenephenylmethylpyrazolone. 2.76 g of 4-phenylethylidenephenylmethylpyrazolone in 50 ml of glacial acetic acid was coupled with diazotized p-nitroaniline (1.45 g). At the end of the addition of the diazo solution the whole mass congealed into a crystalline slurry. Yield 3.1 g (73.0%). Crystallization from glacial acetic acid gave long green needles or prisms, m.p. 235-236°.

0.1005 g sub.: 0.2509 g CO_2; 0.0462 g H_2O. 0.1082 g sub.: 0.2697 g CO_2; 0.0475 g H_2O. 0.1073 g sub.: 15.2 ml N_2 (20°, 764 mm). Found %: C 68.07, 67.97; H 5.10, 4.47; N 16.65. $C_{24}H_{19}O_3N_5$. Calculated %: C 67.76; H 4.47; N 16.47.

4-[α-Phenyl-β-(2'nitro-4'-chlorophenyl)-azo]-ethylidenephenylmethylpyrazolone. 1.73 g of 1-amino-2-nitro-4-chlorobenzene was dissolved in 15 ml of concentrated hydrochloric acid, and the hot solution was poured into ice. 0.69 g of sodium nitrite in 3 ml of water was at once added to the mixture. Urea was added to the solution of the diazo compound formed till a reaction for free nitrous acid was no longer obtained, and the solution was then added dropwise to a solution of 2.76 g of 4-α-phenylethylidenephenylmethylpyrazolone in 50 ml of glacial acetic acid. Almost immediately a precipitate in the form of shining chocolate-colored needles was formed. Yield 2.15 g (47%).

Crystallization from glacial acetic acid gave needles, m.p. 226-227°.

0.1376 g sub.: 0.3130 g CO_2; 0.0505 g H_2O. 0.1553 g sub.: 20.9 ml N_2 (22°, 759 mm). Found %: C 62.03; H 4.07; N 15.52. $C_{24}H_{18}O_3N_5Cl$. Calculated %: C 62.21; H 3.91; N 15.21.

4-[α-Phenyl-β-phenylazo]-ethylidenephenylmethylpyrazolone. A solution of the diazonium salt from 0.93 g of aniline was added to a solution of 2.76 g of phenylethylidenephenylmethylpyrazolone in 30 ml of glacial acetic acid and 0.5 ml of concentrated hydrochloric acid. The reaction mass turned a ruby-red color. 30 ml of water was added to the mass with thorough stirring. The precipitate formed was separated off after 12 hours. Yield 2.64 g (69.8%). Crystallization from alcohol gave reddish-brown leaflets, m.p. 118-120° (decomp.). When heated for a short time to 100° the color of the crystals changed to blue-black, m.p. 118-120°. The substance decomposed when heated for a long time at 100°.

0.1361 g sub.: 0.3621 g CO_2; 0.0743 g H_2O. 0.1436 g sub.: 0.3825 g CO_2; 0.0773 g H_2O. 0.1088 g sub.: 14.0 ml N_2 (21°, 744 mm). Found %: C 72.54, 72.42; H 6.04, 6.04; N 14.63. $C_{24}H_{20}ON_4 \cdot H_2O$. Calculated %: C 72.36; H 5.87; N 14.05.

4-[α-Phenyl-β-(2'-carboxyphenyl)-azo]-ethylidenephenylmethylpyrazolone. 2.76 g of 4-α-phenylethylidenephenylmethylpyrazolone was dissolved in 50 ml of glacial acetic acid and 1.0 ml of concentrated hydrochloric acid. A solution of the diazo compound from 1.37 g of anthranilic acid was added to the solution with cooling and stirring. After 3 hours the precipitate formed was filtered off, washed with alcohol, and dried. Yield 3.47 g (81.8%). Crystallization from glacial acetic acid gave blue-black needles, m.p. 214-215°.

0.1017 g sub.: 0.2821 g C_2O; 0.0439 g H_2O. Found %: C 75.60; H 4.80. $C_{25}H_{20}O_3N_4$. Calculated %: C 75.47; H 4.71.

4-[α-(m-Nitrophenyl)-β-(p-nitrophenyl)-azo]-ethylidenephenylmethylpyrazolone. 1.62 g of m-nitrophenylethylidenephenylmethylpyrazolone was mixed with 30 ml of acetone, and 1.5 ml of concentrated hydrochloric acid was added to the suspension. The yellow precipitate dissolved instantly. The diazo solution prepared from 0.69 g of p-nitroaniline containing 0.5 g of urea was added to the faintly yellow solution. The crystals formed were separated off after 1.5 hours and washed with ether. Yield 1.2 g (51.5%). For purification the substance was dissolved in hot pyridine. The ruby-red solution was filtered and diluted with an equal volume of hot water. On cooling, green needles with a bronze tinge separated out, m.p. 231-232°.

0.1161 g sub.: 18.2 ml N_2 (20°, 762 mm). 0.1245 g sub.: 0.2803 g CO_2; 0.0418 g H_2O. Found %: C 61.43; H 3.84; N 18.10. $C_{24}H_{18}O_5N_6$. Calculated %: C 61.28; H 3.95; N 17.87.

SUMMARY

1. The condensation products of phenylmethylpyrazolone with methyl ketones are capable of reacting with

diazo compounds with the participation of the hydrogen atoms of the methyl groups. This power is displayed only in a mineral acid medium.

2. The increased mobility of the methyl group hydrogens in an acid medium is due to loss of an unshared electron pair by the hetero-nitrogen atom in the ring, and conversion of the substance into an onium salt.

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SYNTHESES AND TRANSFORMATIONS OF PYRIMIDINE DERIVATIVES

V. SULFONATION OF PYRIMIDINE DERIVATIVES

N. V. Khromov-Borisov and R. S. Karlinskaya

By comparison with benzene, pyridine is much less reactive to electrophilic reagents; nitration and sulfonation of pyridine take place with much greater difficulty than in the case of benzene [1]. Because of displacement of the electron cloud to the N hetero-atom, the electron density of all the carbon atoms in the pyridine molecule is decreased. The greatest decrease of electron density is at the α and γ carbon atoms, and therefore the action of electrophilic reagents is directed to the beta-position.

By an extension of this reasoning to the pyrimidine ring it is to be expected that this should be even more inert toward such reagents and that the action of these reagents would be directed to the 5-position.

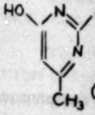
It is not possible either to nitrate or to sulfonate unsubstituted pyrimidine.

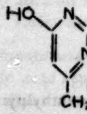
Pyrimidine derivatives with 1st type substituents in the 2,4, or 6 positions should, like the corresponding pyridine derivatives, be nitrated and sulfonated more easily. However, while monohydroxy and monoamino derivatives of pyridine are nitrated in definite conditions [2], it is not possible to nitrate pyrimidine derivatives containing a single hydroxyl group or a single amino group in the even-numbered positions in the ring [3]. A nitro group can be introduced into the 5-position by the action of strong nitrating agents only in the presence of two substituents (OH, NH_2) in the even-numbered positions in the pyrimidine ring. This reaction has great practical importance and is widely used for the synthesis of various pyrimidine derivatives.

The literature contains no information on the sulfonation of pyrimidine derivatives. Only one of our earlier papers [4] includes data on sulfonation of 2,6-dihydroxy-4-methylpyrimidine.

In the present investigation a special study was made of the sulfonation of pyrimidine derivatives containing the following substituents in the molecule: OH, NH_2, CH_3, Cl. These substituents were in the 2,4, and 6 positions of the pyrimidine ring and therefore affected mainly the 5 position, to which, as was already stated, the action of electrophilic reagents is directed.

The following pyrimidine derivatives were sulfonated by the action of chlorosulfonic acid on heating:


(I)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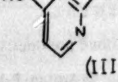
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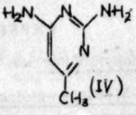
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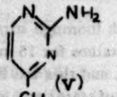
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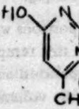
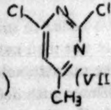

(VI)


(VII)

The compounds (I) [4], (II), (III), and (IV) react relatively easily with chlorosulfonic acid (at 80-130°) to form monosulfonic acids in 34-45% yields. The compounds (II) and (III) which differ by a methyl group in the 4-position, are sulfonated with approximately equal ease. Compounds (V) and (VI), which contain only one substituent, OH or NH_2, are much more difficult to sulfonate. We only succeeded in obtaining, in very low yield (10%) a sulfonated derivative of compound (V); it did not prove possible to isolate the sulfonation product of compound (VI). Dichloromethylpyrimidine (VII) is not changed when heated with chlorosulfonic acid at 100°.

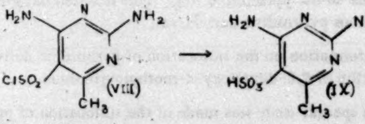
In all the five instances (I-V) monosulfonic acids were obtained. It can be confidently asserted that the sulfonic group in them occupies the 5 position. Furthermore, in compounds (I), (II), and (IV) the 5 position is the only unsubstituted position in the pyrimidine ring. The possibility of the addition of a sulfonic group to nitrogen or oxygen must be excluded; the sulfonic acids obtained were quite stable to hydrolysis; therefore it must be assumed that the SO_3H group enters the same 5 position as is entered by NO_2 and halogens.

All these sulfonic acids are white crystalline substances soluble in alkalies and water. They separate unchanged from the alkaline solutions on acidification. The sulfonic acids from (I), (II), and (III) dissolve with difficulty in cold water and have limited solubility in hot. 2,6-Diamino-4-methyl-5-sulfopyrimidine, and also 2-amino-4-methyl-5-sulfopyrimidine, are much more readily soluble in water. All the substances crystallize from water. The pyrimidine sulfonic acids are insoluble in organic solvents.

The sodium salts of the sulfonic acids from (I), (II), and (III) have better solubility in water than the sulfonic acids themselves. They all swell considerably when heated over a flame. The sodium salts have lower and sharper melting points than the corresponding sulfonic acids. 2-Amino-6-hydroxy-5-sulfopyrimidine chars on heating without melting.

As is known, the reaction of benzene derivatives with excess of chlorosulfonic acid yields the corresponding chlorosulfonates, which are isolated when the reaction mass is poured into water or ice. The pyrimidine compounds studied form sulfonic acids in analogous conditions; chlorosulfonates are not, as a rule, formed. In one instance only – in the sulfonation of 2,6-diamino-4-methylpyrimidine – a chlorosulfonate (VIII) was obtained as the initial reaction product.

To obtain this product, 2,6-diamino-4-methylpyrimidine was sulfonated at 125-130° and the reaction mass was poured over ice. The chlorosulfonate precipitate was immediately filtered off. The chlorosulfonate is readily soluble in warm water, and when the solution is cooled it crystallizes out in the pure state (m.p. 230°). The pure chlorosulfonate is gradually hydrolyzed on boiling in aqueous solution. Dilute mineral acids or alkalies rapidly hydrolyze the chlorosulfonate even in the cold; it is then converted into 2,6-diamino-4-methylpyrimidine-5-sulfonic acid (IX) (m.p. 270-272°, decomp.).



The possibility is not excluded that the sulfonation of other pyrimidine derivatives (I, II, III, V) also first results in the formation of chlorosulfonates which are rapidly hydrolyzed when the reaction mass is diluted with water. However, this question cannot be regarded as solved, especially as the literature also contains instances of chlorosulfonate formation as the result of a secondary reaction – by the action of a second molecule of chlorosulfonic acid on the sulfonic acid [5].

EXPERIMENTAL

2,6-Dihydroxy-4-methyl-5-sulfopyrimidine was described previously [4].

2-Amino-6-hydroxy-4-methyl-5-sulfopyrimidine (II). 2-Amino-6-hydroxy-4-methylpyrimidine was prepared by the condensation of guanidine carbonate with acetoacetic ester in alcohol [6].

4 g of 2-amino-6-hydroxy-4-methylpyrimidine was added in small portions with thorough stirring to 10 ml of chlorosulfonic acid heated to 110°. The reaction mixture was then held at this temperature for 15 minutes and poured into 150 g of ice; a white crystalline precipitate of the sulfonic acid separated out, and this was filtered off and thoroughly washed with water. The mother liquor was diluted with double its volume of water and left to stand. On the next day some more of the sulfonic acid was filtered off. The total yield was 2.7-2.8 g (42-44%). The sulfonic acid does not melt up to 300°, and crystallizes from water.

0.1446 g sub.: 0.1622 g $BaSO_4$. 0.1122 g sub.: 0.1269 g $BaSO_4$. 0.1412 g sub.: 24.4 ml N_2 (19°, 758 mm). 0.1223 g sub.: 21.2 ml N_2 (20°, 760 mm). Found %: S 15.3, 15.5; N 20.0, 20.2. $C_5H_7O_4N_3S$. Calculated %: S 15.6; N 20.4.

The sodium salt was prepared by dissolving 2.05 g of 2-amino-6-hydroxy-4-methyl-5-sulfopyrimidine in a solution of 0.4 g NaOH in 20 ml of water. The solution was evaporated to dryness and the dry residue was recrystallized from water. M.p. 278-280°. The salt is easily soluble in water and insoluble in alcohol.

2-Amino-6-hydroxy-5-sulfopyrimidine (III). 2-Amino-6-hydroxypyrimidine was prepared by the reaction of malic acid with urea in oleum [7].

2 g of 2-amino-6-hydroxypyrimidine was added in small portions, with stirring, to 8 ml of chlorosulfonic acid at 110-115°. The reaction solution was kept at this temperature for 10-15 minutes and poured into 40 g of ice. A white crystalline precipitate of the sulfonic acid gradually separated on external cooling with ice-cold water and rubbing with a glass rod. After 2 hours the precipitate was filtered off, washed thoroughly with water and dried at 80°. Yield 0.85 g (34%). When heated on a metal plate the substance chars slowly without melting. It was purified for analysis by recrystallization from a large volume of water. It may be purified by reprecipitation with hydrochloric acid from alkaline solution.

0.1028 g sub.: 0.1254 g $BaSO_4$. 0.1430 g sub.: 0.1732 g $BaSO_4$. 0.0654 g sub.: 12.2 ml N_2 (21°, 765 mm). 0.1062 g sub.: 19.4 ml N_2 (22°, 772 mm). Found %: S 16.7, 16.5; N 21.6, 21.3. $C_4H_5O_4N_3S$. Calculated %: S 16.7; N 21.9.

The sodium salt was formed by the addition of 0.95 g of 2-amino-6-hydroxy-5-sulfopyrimidine to a solution of 0.2 g of NaOH in 10 ml of water. A slurry was formed, which was evaporated to dryness on a water bath. The weight of the dry residue was 1.03 g. The substance crystallizes from water, m.p. 288-290°.

2,6-Diamino-4-methyl-5-sulfopyrimidine (IV). 2,6-Diamino-4-methylpyrimidine was prepared by the action of alcoholic ammonia under pressure on 2-amino-6-chloro-4-methylpyrimidine [8].

1.6 g of 2,6-diamino-4-methylpyrimidine was added gradually, over a period of 35-40 minutes, to 7 ml of chlorosulfonic acid heated to 125°, with stirring. The reaction solution was kept at 120-130° for 10 minutes and poured into 50 g of ice. A precipitate was gradually formed. The reaction mixture was left to stand and on the following day the precipitated sulfonic acid was filtered off and washed with water. Yield 1.1-1.2 g (40-43%). It was recrystallized from water in the presence of animal charcoal, m.p. 270-272°.

0.1063 g sub.: 0.1224 g $BaSO_4$. 0.0992 g sub.: 0.1141 g $BaSO_4$. 0.1004 g sub.: 24.6 ml N_2 (23°, 760 mm). 0.1004 g sub.: 24.0 ml N_2 (21°, 766 mm). Found %: S 15.6, 15.7; N 27.9, 27.8. $C_5H_8O_3N_4S$. Calculated %: S 15.6; N 27.5.

2,6-Diamino-4-methylpyrimidine-5-chlorosulfonic acid. 1.6 g of 2,6-diamino-4-methylpyrimidine was added at 125-130° with stirring to 7 ml of chlorosulfonic acid over a period of 40 minutes. The reaction mixture was held 10 minutes at this temperature and then poured into a beaker with ice (50 g) cooled with ice-cold water from the outside. The yellowish precipitate of the chlorosulfonate was at once filtered off, rapidly washed with ice-cold water twice (15-20 ml water each time) and dried at 40-50°. Yield 1.0 g (36%). To purify the product it was dissolved in warm water (60-80°), a little animal charcoal was added, the solution filtered, the colorless solution cooled rapidly, and the dazzling white crystals of the chlorosulfonate separated off, m.p. 228-230°.

0.1096 g sub.: 23.2 ml N_2 (19°, 763 mm). 0.1024 g sub.: 22.1 ml N_2 (20°, 760 mm). Found %: N 24.8, 24.9. $C_5H_7O_2N_4SCl$. Calculated %: N 25.2.

The chlorosulfonate was hydrolyzed by boiling 0.2 g of it in 10 ml of water. After 15 minutes of boiling, traces of hydrochloric acid appeared in the solution. After 1 hour the hydrolysis was complete; the hydrochloric acid was precipitated by silver nitrate, the precipitate filtered off, and the filtrate boiled for another 30 minutes. No hydrochloric acid was detected in this solution. The solution was evaporated to dryness, and the dry residue recrystallized from water, m.p. 270°. A sample mixed with 2,6-diamino-4-methyl-5-sulfopyrimidine showed no depression of melting point.

The alkaline hydrolysis of the chlorosulfonate was carried out by dissolving a weighed portion with gentle heating in 0.1 N caustic soda solution. After 1 hour the solution was back-titrated with 0.1 N hydrochloric acid solution.

0.1226 g sub.: 10.8 ml 0.1 N. NaOH. $C_5H_7O_2N_4SCl$. Calculated: 11.0 ml 0.1 N NaOH.

2-Amino-4-methyl-5-sulfopyrimidine (V). 2-Amino-4-methylpyrimidine was prepared by the reduction of 2-amino-6-chloro-4-methylpyrimidine with zinc dust [9].

5 g of 2-amino-4-methylpyrimidine was added at 115° with stirring to 12 ml of chlorosulfonic acid. After

40 minutes the reaction solution was poured into 75 g of ice. The solution was then diluted with one and a half times its volume of water and left to stand. After 2 months a yellowish crystalline precipitate separated out. Yield 0.7 g (10%). The substance melts and swells when heated on a metal plate. It begins to darken at 230° and gradually decomposes. It crystallizes from water to form small shiny crystals.

0.0682 g sub.: 0.0830 g $BaSO_4$. 0.0821 g sub.: 0.0996 g $BaSO_4$. Found %: S 16.7, 16.6. $C_5H_7O_3N_3S$. Calculated %: S 17.0.

SUMMARY

1. The sulfonation of pyrimidine derivatives containing two substituents (OH, NH_2) in the 2,4, or 6 positions, takes place relatively easily. Monosulfonic acids with a sulfo group in the 5 position are formed. 2-Amino-6-hydroxy-4-methyl-5-sulfopyrimidine, 2-amino-6-hydroxy-5-sulfopyrimidine, and 2,6-diamino-4-methyl-5-sulfopyrimidine were prepared.

2. In the action of chlorosulfonic acid on 2,6-diamino-4-methylpyrimidine the first reaction product is 2,6-diamino-4-methylpyrimidine-5-chlorosulfonic acid, which readily passes into 2,6-diamino-4-methyl-5-sulfopyrimidine.

3. The sulfonation of pyrimidine derivatives with only one hydroxy or amino group is much more difficult. 2-Amino-4-methyl-5-sulfopyrimidine was prepared in 10% yield.

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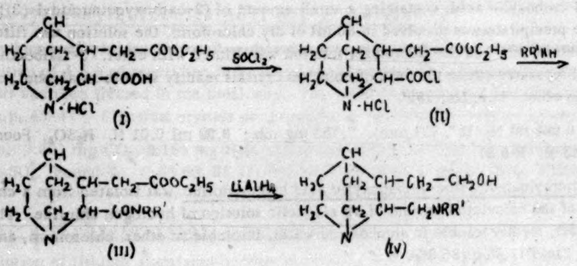
SYNTHESIS OF SUBSTITUTED 2-AMINOMETHYL-3-(β-HYDROXYETHYL)-QUINUCLIDINES

M. V. Rubtsov, E. E. Mikhlina, and V. Ya. Furshtatova

In the previous communications the synthesis of [2-carboxyquinuclidyl-(3)]-acetic acid, a number of its derivatives, and also of some substituted 2-aminomethyl-3-(β-aminoethyl)-quinuclidines was described [1, 2].

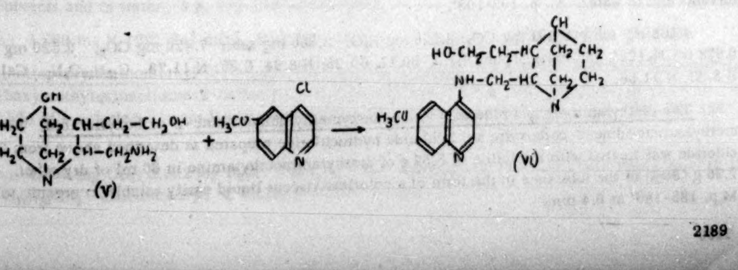
In further studies of the properties of 2,3-disubstituted quinuclidines it was found that the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid is readily hydrolyzed on standing in aqueous solution to form the acid ester. It was also found that the ethyl ester of quinuclidine-2-carboxylic acid is also easily hydrolyzed in such conditions to give quinuclidine-2-carboxylic acid. Consideration of the properties of these esters suggests that the carboethoxyl group in the 2 position of the quinuclidine nucleus is saponified in the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid, and the semi-ester formed by hydrolysis has the structure of 3-carboethoxymethylquinuclidine-2-acetic acid (I).

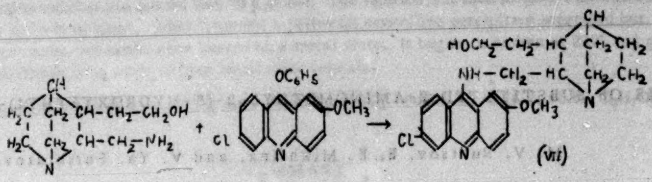
This last was used to synthesize a number of 2-alkyl(aryl)aminomethyl-3-(β-hydroxyethyl)-quinuclidines according to the scheme:



The hydrochloride of 3-carboethoxymethylquinuclidine-2-carboxylic acid (I) was converted with the aid of thionyl chloride into the acid chloride (II), which was then treated with alkyl or aryl amines. The alkyl or aryl amides of 3-carboethoxymethylquinuclidine-2-carboxylic acid (III) so formed were reduced by lithium aluminum hydride to the 2-alkyl(aryl)aminomethyl-3-(β-hydroxyethyl)-quinuclidines (IV). The following alkyl(aryl) amines were used for the synthesis of the amides (III): diethylaminoethylamine, diethylaminoisopentylamine, 2-aminopyridine, piperidine, 6-methoxy-4-aminoquinoline, and 2-methoxy-6-chloro-9-aminoacridine. However, the last two compounds could not be acylated with the acid chloride of 3-carboethoxymethylquinuclidine-2-carboxylic acid, and the corresponding amides (III) could not be prepared in this way.

Derivatives of 2-aminoethylquinuclidine containing quinoline (VI) and acridine (VII) ring systems were obtained by the reaction of 2-aminomethyl-3-(β-hydroxyethyl)-quinuclidine (V) with 6-methoxy-4-chloroquinoline and 2-methoxy-6-chloro-9-phenoxyacridine:





(VII)

The reaction between (V) and 4-chloro-6-methoxyquinoline was carried out in phenol at 180-190°, and the reaction with 2-methoxy-6-chloro-9-phenoxyacridine in boiling butyl alcohol.

EXPERIMENTAL

3-Carboethoxymethylquinuclidine-2-carboxylic acid

13.4 g of the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid was dissolved in 250 ml of water and the solution was left at room temperature for 7 days. The water was then distilled off under vacuum and the residue dried by 4 additions and removals of benzene. The solid residue was dissolved on warming in 20 ml of anhydrous alcohol, the alcoholic solution was filtered to remove the turbidity, and 150 ml of anhydrous ether was added. The colorless crystals which formed were filtered off and washed with ether. The yield was 11.35 g of 3-carboethoxymethylquinuclidine-2-carboxylic acid, containing a small amount of [2-carboxyquinuclidyl-(3)]-acetic acid. To remove the latter, the precipitate was dissolved in 50 ml of dry chloroform, the solution was filtered to remove the di-acid insoluble in chloroform, and the chloroform solution was diluted with ether. 3-Carboethoxymethylquinuclidine-2-carboxylic acid separated out in the form of colorless crystals readily soluble in alcohol, chloroform, and water, and insoluble in ether. M.p. 180-182°.

4.709 mg sub.: 0.245 ml N_2 (19°, 731 mm). 7.755 mg sub.: 3.29 ml 0.01 N. H_2SO_4. Found %: N 5.85, 5.94. $C_{12}H_{19}O_4N$. Calculated %: N 5.81.

3-Carboethoxymethylquinuclidine-2-carboxylic acid hydrochloride was isolated from a chloroform solution of the base by means of the calculated amount of an alcoholic solution of hydrogen chloride. The substance is a white crystalline powder, readily soluble in alcohol and water, insoluble in ether, chloroform, and acetone. M.p. 228-229° (decomp.). Yield 11.85 g (85.8%).

3.498 mg sub.: 6.618 mg CO_2; 2229 mg H_2O. 4.015 mg sub.: 7.678 mg CO_2; 2.578 mg H_2O. 9.003 mg sub.: 0.410 ml N_2 (23°, 728 mm). 8.755 mg sub.: 0.393 ml N_2 (23°, 728 mm). Found %: C 51.63, 52.18; H 7.13, 7.18; N 5.04, 4.96. $C_{12}H_{20}O_4NCl$. Calculated %: C 51.89; H 7.21; N 5.04.

3-Carboethoxymethylquinuclidine-2-carboxylic acid amide. 4.7 g of 3-carboethoxymethylquinuclidine-2-carboxylic acid hydrochloride and 47 ml of thionyl chloride were heated together at 60-65° for 4 hours. The precipitate dissolved completely during this time. The thiomyl chloride was distilled off under vacuum, and its last traces were removed by 3-fold addition of benzene followed by its removal under vacuum. The colorless precipitate of the 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride was suspended in 50 ml of dry ether and a stream of ammonia passed into the suspension for 2 hours. The reaction mass was treated with 40 ml of 50% potash solution and extracted with chloroform. The chloroform solution was dried with potash, the chloroform was distilled off under vacuum, and the solid residue recrystallized from dry ether. The yield was 3.65 g (89.6%) of 3-carboethoxymethylquinuclidine-2-carboxylic acid amide in the form of colorless crystals easily soluble in organic solvents and in water. M. p. 102-103°.

4.168 mg sub.: 9.191 mg CO_2; 3.220 mg H_2O. 3.350 mg sub.: 7.420 mg CO_2; 2.520 mg H_2O. 5.970 mg sub.: 0.628 ml N_2 (22°, 735 mm). Found %: C 60.17, 60.26; H 8.64, 8.39; N 11.78. $C_{12}H_{20}O_3N_2$. Calculated %: C 60.00; H 8.33; N 11.66.

The diethylaminoethylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid. The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared as described above from 3 g of the acid hydrochloride was treated with a solution of 5.52 g of diethylaminoethylamine in 60 ml of dry ether. The yield was 2.95 g (80%) of the substance in the form of a colorless viscous liquid easily soluble in organic solvents and in water. M.p. 185-186° at 0.4 mm.

3.384 mg sub.: 7.861 mg CO_2; 2900 mg H_2O. 3.110 mg sub.: 7.239 mg CO_2; 2.793 mg H_2O. 6.375 mg sub.: 0.720 ml N_2 (22.5°, 729 mm). 9.640 mg sub.: 1.062 ml N_2 (22.5°, 734 mm). Found %: C 63.39, 63.52; H 9.58, 10.04; N 12.55, 12.35. $C_{18}H_{33}O_3N_3$. Calculated %: C 63.72; H 9.73; N 12.4.

The diethylaminoisopentylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid. The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared from 2.5 g of the acid hydrochloride was added to a solution of 4.28 g of diethylaminoisopentylamine in 30 ml of anhydrous ether. The appropriate treatment yielded 2.62 g of the amide (76.1%), b.p. 190-191° at 0.3 mm. It is a viscous greenish liquid with a strong amine odor, easily soluble in organic solvents, less easily in water.

3.911 mg sub.: 9.433 mg CO_2; 3.601 mg H_2O. 5.710 mg sub.: 0.557 ml N_2 (22°, 739 mm). Found %: C 65.82; H 10.30; N 10.98. $C_{21}H_{39}O_3N_3$. Calculated %: C 66.14; H 10.23; N 11.00.

The pyridyl-(2')-amide of 3-carboethoxymethylquinuclidine-2-carboxylic acid. The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared from 3 g of the acid chloride was treated with 6.1 g of pyridine in 40 ml of anhydrous benzene at room temperature. In fractionation of the reaction products the pyridine was first driven off under a pressure of 10 mm, and the amide was then distilled. B.p. 210-212° at 0.3 mm. It is an extremely viscous yellow liquid which crystallizes when rubbed with a rod. The crystals melt at 56-58° after being washed in petroleum ether. They are easily soluble in ether, benzene, acetone, and alcohol, and with difficulty in water. Yield 2.4 g (70.2%).

3.711 mg sub.: 8.708 mg CO_2: 2.381 mg H_2O. 3.708 mg sub.: 8.766 mg CO_2; 2.504 mg H_2O. 4.088 mg sub.: 0.494 ml N_2 (25°, 733 mm). Found %: C 64.03, 64.51; H 7.18, 7.55; N 13.34. $C_{17}H_{23}O_3N_3$. Calculated %: C 64.35; H 7.25; N 13.25.

N-[3-carboethoxymethylquinuclidinoyl-(2)]-piperidine

The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared from 3 g of the acid was added to a solution of 4.5 g of piperidine in 30 ml of dry benzene. The reaction mass was heated on a water bath at 60-70° for 3 hours and then treated in the usual way. The yield was 1.95 g (50.8%) of a substance with b.p. 160-162° at 0.4 mm, m.p. 45-47°. Colorless crystals easily soluble in water and in organic solvents.

3.932 mg sub.: 9.601 mg CO_2; 3.161 mg H_2O. 3.215 mg sub.: 7.795 mg CO_2; 2.598 mg H_2O. 9.490 mg sub.: 6.02 ml 0.01 N H_2SO_4. Found %: C 66.63, 66.17; H 9.00, 9.04; N 8.88. $C_{17}H_{28}O_3N_2$. Calculated %: C 66.25; H 9.09; N 9.09

2-Aminomethyl-3-(β-hydroxyethyl)-quinuclidine

2.4 g of a solution of lithium aluminum hydride in 60 ml of anhydrous ether was added to a solution of 3.65 g of carboethoxymethylquinuclidine-2-carboxylic acid amide in 80 ml of anhydrous benzene. The reaction mass was kept heated at the boil for 20 hours. The excess $LiAlH_4$ was then decomposed by 4 ml of water, and the precipitate was filtered off and washed with benzene. The combined solutions were dried with potash and evaporated under a vacuum; the residue was distilled. B.p. 157-160° at 0.3 mm. Yield 2.2 g (78.7%).

2-Aminomethyl-3-(β-hydroxyethyl-quinuclidine is a colorless viscous liquid easily soluble in organic solvents. It was identified as the picrate, m.p. 202-204°.

4.352 mg sub.: 6.528 mg CO_2; 1.652 mg H_2O. 6.327 mg sub.: 1.000 ml N_2 (24°, 744 mm). Found %: C 40.94; H 4.25; N 17.78. $C_{10}H_{20}ON_2 \cdot 2C_6H_3O_7N_3$. Calculated %: C 41.15; H 4.05; N 17.43.

2-Diethylaminoethylaminomethyl-3-(β-hydroxyethyl)-quinuclidine. 2.4 g of the diethylaminoethylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid was reduced by 0.82 g of lithium aluminum hydride in 65 ml of ether, as described above. The yield was 1.3 g (65%) of a viscous greenish liquid with a weak amine odor, easily soluble in organic solvents and in water. B.p. 170-172° at 0.35 mm.

8.290 mg sub.: 1.069 ml N_2 (22°, 741 mm). Found %: N 14.56. $C_{16}H_{33}ON_3$. Calculated %: N 14.84.

2-Diethylaminoisopentylaminomethyl-3-(β-hydroxyethyl)-quinuclidine. 3.8 g of the diethylaminoisopentylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid was reduced by 1.2 g of $LiAlH_4$ in 80 ml of ether. The yield was 2.8 g (86.5%) of a colorless viscous liquid, easily soluble in organic solvents and in water. B.p. 185-186° at 0.3 mm.

3.651 mg sub.: 9.390 mg CO_2; 3.912 mg H_2O. 7.445 mg sub.: 0.840 ml N_2 (23°, 749 mm). Found %: C 70.18; H 11.98; N 12.83. $C_{19}H_{39}ON_3$. Calculated %: C 70.16; H 12.00; N 12.91.

2-[Pyridyl-(2')-aminomethyl]-3-(β-hydroxyethyl)-quinuclidine. 4.35 g of the pyridyl-(2')-amide of 3-carboethoxymethylquinuclidine-2-carboxylid acid was reduced by 2.16 g of $LiAlH_4$ in a mixture of 60 ml of ether and 70 ml of benzene. The amine formed was extracted with chloroform. Evaporation of the solvent yielded 2.5 g (69.8%) of a substance with m.p. 137-139°. The compound consists of small pale yellow crystals, easily soluble in alcohol and chloroform, difficultly soluble in benzene, insoluble in ether, soluble in water upon gentle heating.

3.799 mg sub.: 9.570 mg CO_2; 2.950 mg H_2O. Found %: C 68.75; H 8.68. $C_{15}H_{23}ON_3$. Calculated %: C 69.00; H 8.81.

N-[3-(β-hydroxyethyl)-quinuclidineaminomethyl-(2)]-piperidine

2.35 g of N-[3-carboethoxymethylquinuclidinoyl-(2)]-piperidine was reduced by 1.2 g of $LiAlH_4$ in a mixture of 50 ml of ether and 50 ml of benzene. The yield was 1.3 g (67.6%) of a white crystalline powder, easily soluble in chloroform, alcohol, and acetone, difficultly soluble in cold water and easily in hot. After recrystallization from benzene the amine melts at 116-117°.

4.800 mg sub.: 12.555 mg CO_2; 4.765 mg H_2O. 7.366 mg sub.: 5.67 ml 0.01 N H_2SO_4. Found %: C 71.38; H 11.11; N 10.78. $C_{15}H_{28}ON_2$. Calculated %: C 71.43; H 11.11; N 11.11.

2-[6'-Methoxyquinolyl-(4')]-aminomethyl-3-(β-hydroxyethyl)-quinuclidine

1.25 g of 2-aminomethyl-3-(β-hydroxyethyl)-quinuclidine, 1.31 g of 6-methoxy-4-chloroquinoline, and 15 g of redistilled phenol were heated together on an oil bath at 190° for 3 hours. The cooled reaction mass was poured into 50 ml of 20% caustic soda solution and extracted with chloroform. The chloroform solution was dried with potash, the chloroform was distilled off, and the remaining oily crystals were triturated with ether. The residue was filtered off, washed with a small quantity of chloroform, and then recrystallized from a mixture of chloroform and ether (1 : 6). The yield was 1.5 g (46.6%) of colorless crystals easily soluble in alcohol and chloroform and insoluble in ether or water. M.p. 207-209°.

7.900 mg sub.: 0.838 ml N_2 (25°, 728 mm). Found %: N 11.68. $C_{20}H_{27}O_2N_3$. Calculated %: N 12.01.

2-{[2'-Methoxy-6'chloroacridyl-(9')]-aminomethyl} -3-(β-hydroxyethyl)-quinuclidine

0.62 g of 2-aminomethyl-3-(β-hydroxyethyl)-quinuclidine, 0.96 g of 2-methoxy-6-chloro-9-phenoxyacridine and 25 ml of n-butyl alcohol were heated together on an oil bath at 125-130° for 23 hours. The butyl alcohol was distilled off under vacuum, the residue was dissolved in 20 ml of ether, and the ether solution deposited 0.96 g of a substance after standing for 1 hour. The substance was crystallized from 20 ml of 50% alcohol. The result was bright yellow crystals, easily soluble in alcohol and chloroform, insoluble in ether or water. M.p. 165-166.5°. Yield 78.3%.

3.131 mg sub.: 7.782 mg CO_2; 1.820 mg H_2O. 8.080 mg sub.: 0.678 ml N_2 (23°, 756 mm). Found %: C 67.82; H 6.50; N 9.62. $C_{24}H_{28}O_2N_3Cl$. Calculated %: C 67.70; H 6.58; N 9.87.

The substance was converted into the hydrochloride, which was in the form of yellow crystals easily soluble in water, difficultly in alcohol, insoluble in ether or acetone. M.p. 258-260° (decomp.).

4.099 mg sub.: 3.602 mg AgCl. Found %: Cl 21.74. $C_{24}H_{28}O_2N_3Cl \cdot 2HCl$. Calculated %: Cl 21.36.

SUMMARY

Hydrolysis of the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid yielded 3-carboethoxymethylquinuclidine-2-acetic acid. This was used for the synthesis of a number of 2-alkyl(aryl)aminomethyl-3-(β-hydroxyethyl)-nuclidines.

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• T. p. = C. B. Translation pagination.

APPLICATION OF INFRARED ABSORPTION SPECTRA TO INVESTIGATION OF THE INTERMEDIATE PRODUCTS OF VITAMIN A AND CAROTENE SYNTHESIS

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The infrared spectra of certain compounds of the polyene series, prepared synthetically, were studied. Infrared spectra can provide valuable information on the structure of these compounds, and in addition investigation of the infrared spectra of the reaction products can serve as a method for determining the extent to which any given stage of the synthesis has been completed.

The absorption spectra in the infrared region were measured with a Hilger spectrometer D-209, the single-beam model being used. The source of light was a saltpeter rod heated to 1140°. The measurements were carried out in the region between 2.5 and 15 μ with the aid of a rock salt prism. Rock salt plates were used for the cells. The thickness of the layer of substance under investigation was regulated by layers of aluminum foil, and was 10, 20, 30 and 70 μ. Exact regulation of the layer thickness, however, was difficult because of the high viscosity of the substances studied.

I. The infrared spectrum of pseudoionone. Pseudoionone is a starting material for the preparation of β-ionone, which forms the basis of all known syntheses of vitamin A and carotenoids. We studied the infrared spectra of pseudoionone synthesized from methylheptenone [1] (Fig. 1a) and also of pseudoionone prepared from natural citral (Fig.1b). Both the pseudoionones were redistilled under vacuum (0.1 mm Hg) before determination of their spectra. The spectra of the two pseudoionones coincide almost completely. The greatest interest is presented by the vibration forms of the components of the intense triplet band in the region 1675-1590 cm^{-1}. The 1675 cm^{-1} absorption band evidently corresponds to the vibration frequency of the C= O carbonyl group conjugated with two double carbon-carbon bonds, as a result of which it is much lower than the vibration frequency of the carbonyl group in aliphatic ketones, 1720 cm^{-1} [2]. Because of conjugation, the frequency of the C= O double bond is similarly lowered; this corresponds to the absorption band in the 1590 cm^{-1} region, while the isolated double bond at the end of the chain corresponds to the absorption band at 1635 cm^{-1}.

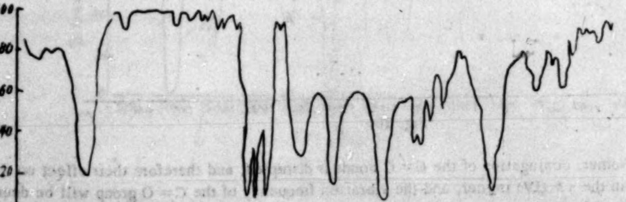
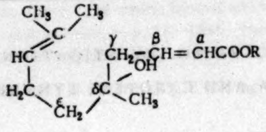


Fig. 1a

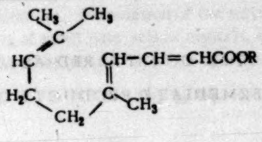
Thus, the sepctra of synthetic pseudoionone support the view that its structure is correctly described by the generally accepted formula. There are, however, some differences between the spectra of the pseudoionones obtained from different starting materials.

1. The 1700 cm^{-1} absorption band is found only in the spectrum of pseudoionone synthesized from methylheptenone. This band corresponds to the vibration frequency of the carbonyl bond, somewhat lower than the C= O vibration frequency in ketones of the aliphatic series. Its presence in the spectrum of the pseudoionone can only be explained by the presence of admixtures of substances the molecules of which do not have such strong conjugation of the carbon-carbon double bonds as exists in pseudoionone, where the C= O bond is conjugated with a chain consisting of two conjugated carbon-carbon bonds. It must be remembered that in the synthesis of pseudoionone from methylheptenone by condensation of the latter with γ-bromocrotonic ester, a hydroxy ester (I) is obtained, which can split

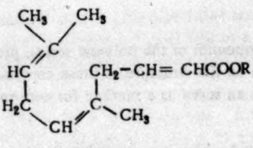
off water to give isomers with the double bond in the $\gamma\delta$ and $\delta\epsilon$ positions (II) and (III):



(I)

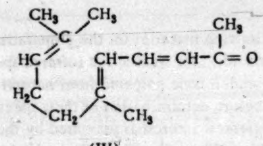


(II)

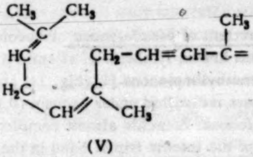


(III)

and consequently the pseudoionone which is formed later can also be obtained in two isomeric forms, $\gamma\delta$ (IV) and $\delta\epsilon$ (V):



(IV)



(V)

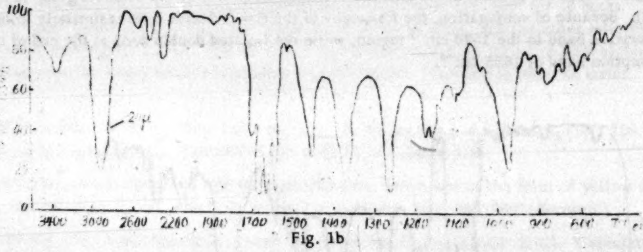


Fig. 1b

In the $\delta\epsilon$ (V) isomer, conjugation of the C= C bonds is disrupted, and therefore their effect on the CO group is rather weaker than in the $\gamma\delta$ (IV) isomer, and the vibration frequency of the C= O group will be decreased less by the influence of one C= C bond conjugated with it. Thus, in the molecule of 2-methylbutene-1-one-3 the C= O group is conjugated with only one C= C group, and in the spectrum of this substance [3] the C= O group is represented by an absorption band at 1700 cm^{-1}, in just the region in which an absorption band is found in the spectrum of pseudoionone synthesized from methylheptenone.

Evidently, the main mass of the pseudoionone formed in the synthesis is the $\gamma\delta$-isomer, as is shown by the presence in its spectrum of a very intense band at 1675 cm^{-1}, which corresponds to a C= O group conjugated with two C= C bonds, and only a small percentage of the $\delta\epsilon$-isomer is obtained, as the corresponding C= O band at 1700 cm^{-1} in the spectrum of synthetic pseudoionone has low intensity.

2. The absorption band at 882 cm^{-1} in the spectrum of pseudoionone synthesized from methylheptenone is more intense than the 815 cm^{-1} band, while these two bands have the same intensity in the spectrum of pseudoionone synthesized from natural citral. Absorption bands in the 880 cm^{-1} region are characteristic of cis-isomers [4]. We

may therefore conclude that pseudoionone synthesized from methylheptenone contains more cis-isomer than the pseudoionone synthesized from natural citral.

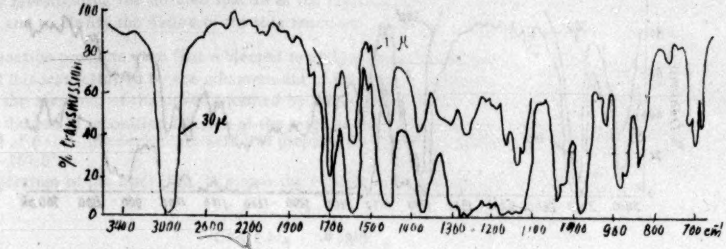


Fig. 2.

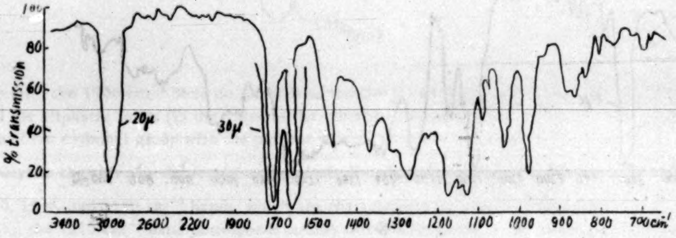


Fig. 3.

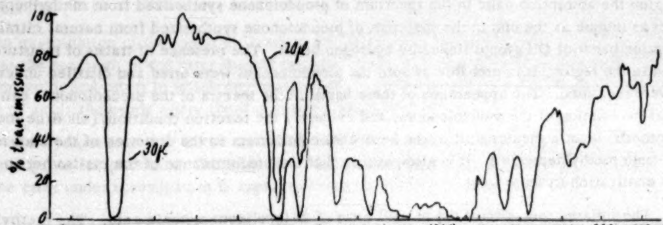


Fig. 4.

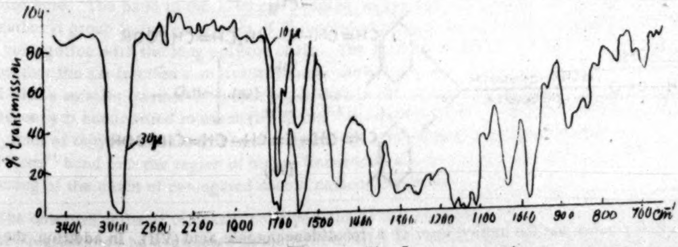


Fig. 5.

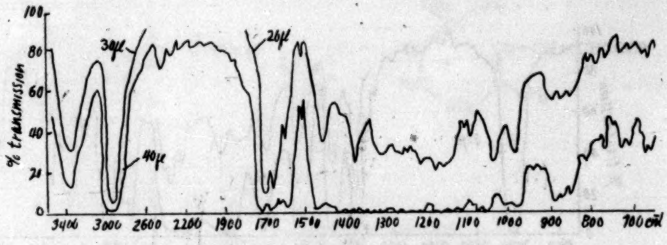


Fig. 6.

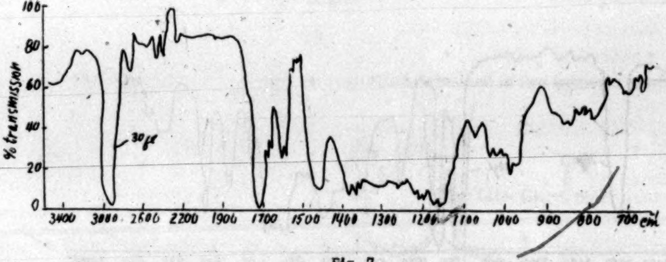
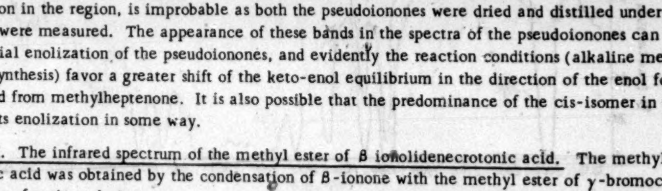


Fig. 7.

3. A fairly considerable difference between the sepctra of the pseudoionones is found in the 3400 cm^{-1} region. In this region the absorption band in the spectrum of pseudoionone synthesized from methylheptenone is approximately 3 times as intense as the one in the spectrum of pseudoionone synthesized from natural citral. This region contains the absorption bands of OH groups linked by hydrogen bonds. The presence of traces of moisture, which might cause absorption in the region, is improbable as both the pseudoionones were dried and distilled under vacuum before the sepctra were measured. The appearance of these bands in the spectra of the pseudoionones can be attributed only to the partial enolization of the pseudoionones, and evidently the reaction conditions (alkaline medium at the last stage of the synthesis) favor a greater shift of the keto-enol equilibrium in the direction of the enol form in pseudoionone obtained from methylheptenone. It is also possible that the predominance of the cis-isomer in this pseudoionone favors its enolization in some way.

II. The infrared spectrum of the methyl ester of β ionolidenecrotonic acid. The methyl ester of β-ionolidenecrotonic acid was obtained by the condensation of β-ionone with the methyl ester of γ-bromocrotonic acid in the presence of activated zinc:



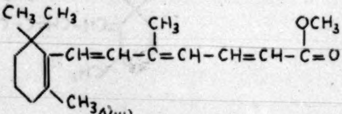
The main reaction product was the methyl ester of β-ionolidenecrotonic acid (VII). In addition, the reaction mixture contained unchanged β-ionone.

Most workers report the yield of crystalline β-ionolidenecrotonic acid by this reaction as 7.5-10% of theoretical. Evidently, the yield is greatly decreased by side reactions. The great similarity between the properties of the reaction products indicates the formation of a number of isomeric compounds.

Separation of the reaction products and their identification by chemical methods presents considerable difficulties. By investigating the infrared spectra of the reaction products we attempted to determine the mechanism of the reaction and to clarify the nature of the side reactions.

The reaction products were first subjected to chromatographic separation with the aid of aluminum oxide column, and this was followed by the measurement of the infrared spectra of 4 consecutive chromatographic fractions. In addition, the spectrum of the product formed by the action of diazomethane on an ether solution of the acids obtained from the easily saponified fraction of the original ester was measured. The standard comparison sample of the methyl ester of β-ionolidenecrotonic acid was prepared by the action of diazomethane on the pure crystalline acid of m.p. 156-157.5°.

The spectrum of the ester (Fig. 2) proves the validity of formula (VIII):



(VIII)

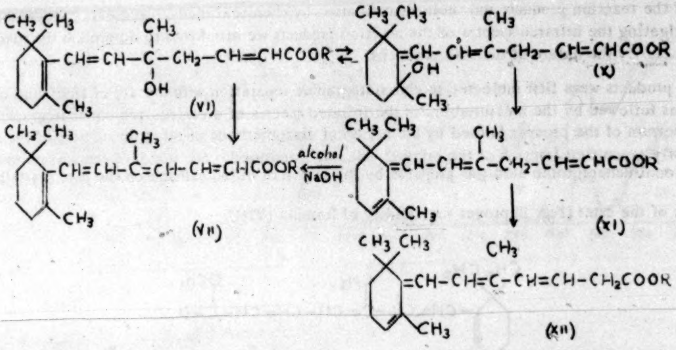
In fact, the 1700 cm^{-1} band corresponds to the C= O carbonyl group in the ester grouping. In comparison with esters of the aliphatic series [2] the value of the vibration frequency for C= O is decreased by 45 cm^{-1} due to conjugation of the carbonyl group with the polyene chain. The vibration frequency of the C=C linkage at 1600 cm^{-1} in the polyene chain is also decreased as the result of conjugation. The ester grouping C−O−CH_3 corresponds to the 1270, 1200, and 1170 cm^{-1} bands, which are characteristic for methyl esters of acids with long carbon atom chains [5]; the 1270 cm^{-1} band corresponds mainly to vibration of the C−O bond in the ester group, while the 1200 and 1170 cm^{-1} bands correspond to deformational vibration of the whole ester group. The 1140 cm^{-1} band also evidently owes its appearance in the spectrum to one of the vibrational forms of the ester group, as it is found in the spectra of many esters [3].

In addition, an examination of the spectrum leads to the conclusion that the C−O− linkage is conjugated with the polyene chain, as the spectrum of the ester studied contains bands at 1040 and 1020 cm^{-1}, which are found in the spectra of unsaturated acids and esters in which conjugation between C−O− and C= C bonds exists, and are not found in the spectra of acids and esters where there is no such conjugation.

The presence of a cyclohexene ring in the ester molecule is proved by the existence of bands in the 1130, 1450, and 1650 cm^{-1} regions [3] in its spectrum. The 1650 cm^{-1} band is masked by the 1700 and 1600 cm^{-1} bands. With a thinner layer of the ester under investigation it appears as a small shoulder on the right-hand slope of the 1700 cm^{-1} absorption band.

The spectrum of the 1st fraction (Fig. 3) obtained by chromatography from technical ethyl ester of β-ionolidenecrotonic acid shows certain changes when compared with the spectrum of the standard ester. The broad intense absorption band in the 1700 cm^{-1} region has two maxima at 1700 and 1720 cm^{-1}. Two absorption bands are probably superposed here. The band in the 1700 cm^{-1} region, as has already been stated, corresponds to the vibration frequency of the carbonyl group in the ethyl ester of β-ionolidenecrotonic acid, lowered considerably (by 45 cm^{-1}) by the effect of conjugation with the long polyene chain. The position of the second maximum in the 1720 cm^{-1} region indicates that the 1st fraction contains substances similar to ethyl crotonate, in which the carbonyl group is conjugated with a smaller number of double bonds than in the ester of β-ionolidenecrotonic acid, and therefore its vibration frequency is not lowered so much (by 25 cm^{-1} instead of 45 cm^{-1}). In fact, the C= O group absorption band in the spectrum of ethyl crotonate lies in this region [3]. This view is also supported by the shift of the maximum of the 1610 cm^{-1} band into the region of higher frequencies relative to the standard ester (1610 cm^{-1}), which indicates a shortening of the chain of conjugated double carbon-carbon bonds.

The observed shifts of the bands corresponding to the vibrations of the C= O and C=C groups into the higher frequency regions may be considered in the light of allyl and prototropic regroupings which accompany dehydration:



In the ester (XI), which is isomeric with the β-ionolidenecrotonic ester, and which is formed as a side product, the C= O group is conjugated with only one C= C double bond, as in the crotonic ester. The chain of conjugated C= C bonds in the ester (XI) is shorter than this chain in the ester (VIII). The yield of the β-ionolidenecrotonic ester is partly decreased owing to allyl regroupings. The hypothesis that allyl regroupings accompany the reaction by which the β-ionolidenecrotonic ester is formed, which we put forward as the result of a study of the infrared spectra of the reaction products, was also proposed by a number of workers who studied analogous reactions [6].

The spectra of the 2nd and 3rd fractions (Fig. 4 and 5) are very similar to the spectrum of the 1st fraction, and all that has been said about the 1st fraction applies to them also.

The spectrum of the 4th fraction (Fig. 6) differs very significantly from the spectrum of the pure ester. Firstly, the spectrum of the 4th fraction contains a very intense broad band in the 3380 cm^{-1} region which is characteristic of compounds with hydroxyl groups associated by means of hydrogen bonds. The presence of bands characteristic of the cyclohexene ring in the spectrum of this fraction, together with the hydroxyl group band, indicates the presence of residues of the non-hydrated hydroxy ester (VI). This view is apparently contradicted by the position of the carbonyl group absorption band in the 1700 cm^{-1} region, which is 20 cm^{-1} below its position in the spectrum of ethyl crotonate (1720 cm^{-1}), where the C= O group is conjugated with one C= C group, as in the case of the hydroxy ester (VI). However, this may be explained by the supposition that the carbonyl groups of one molecule are joined by hydrogen bonds to hydroxyl groups of another, and the vibration frequency of these groups is lowered due to the hydrogen bond.

In the spectrum of the substance obtained by the action of diazomethane on an ether solution of the acids synthesized from the easily saponifiable portion of the original ester the carbonyl group band lies in the 1730 cm^{-1} region. This indicates that the carbonyl group is not conjugated with the polyene chain, the presence of which in the molecules of this substance is shown by the 1600-1585 cm^{-1} absorption band.

Such compounds of the type (XII) may be formed as the result of allyl and prototropic regroupings which accompany dehydration under the action of alkaline agents.

The general similarity between the spectra of the substances studied shows the presence of a mixture of compounds with the same structural elements but differing in the positions of the latter and in the degree of double bond conjugation. The results indicate the formation of structural isomers of β-ionolidenecrotonic acid during condensation of β-ionone with esters of γ-bromocrotonic acid in the presence of zinc, by the Reformatsky reaction.

SUMMARY

A study was made of the infrared spectra of pseudoionones synthesized from methylheptenone and from natural citral, and also of the methyl ester of β-ionolidenecrotonic acid and four consecutive fractions obtained by its chromatographic purification.

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THE MICROSTRUCTURE OF PROTEINS

XIII. THE BEHAVIOR OF DIACETYLDIKETOPIPERAZINE IN ITS REACTIONS WITH AMINES

R. G. Petrova, L. N. Akimova, and N. I. Gavrilov

The reaction of diacetyldiketopiperazine with amines was first described by Bergmann, when it was shown that when amines act on acetylated diketopiperazine [1], and also on acetylated histidine [2], theobromine [2], and other amides [3], acetyl or benzoyl groups pass from the amides to the amines. A similar transformation was observed by Bergmann by the action of arginine base in alcohol on diacetyldiketopiperazine [1]. The transacetylation was accompanied by decomposition of diacetyldiketopiperazine with the formation, first, of N,N'-diacetylglycylglycine, which was then converted into N-acetylglycylglycine by the removal of an acetyl group from nitrogen. In Bergmann's view, acyl-substituted amides, such as diacetyldiketopiperazine, are capable of acylating compounds with free or substituted amino groups. A similar process was also observed by Bergmann in the case of acylated ketoheteroamide rings. Even prior to Bergmann's work in 1924-1927, Brunner [4] studied the transformations of diacyl amides by the action of various amines. However, in these researches, in contrast to those of Bergmann, the intermediate reaction products were isolated and shown to be amidines. The results of these researches prompted us to repeat the experiments of Brunner and Bergmann with diacetyldiketopiperazine which, according to Brunner, should lead to the formation of an amidine. Such experiments were carried out by the present authors [5] with diacetyldiketopiperazine and esters of amino acids (glycine, tyrosine); a careful study of the reaction products showed convincingly that the reaction proceeds in two directions, noted by Bergmann and earlier by Brunner. Thus, in addition to the transacetylation reaction, the formation of an acetylated amidine was shown. Later the mechanism of this reaction was established and its possible directions in accordance with the medium chosen indicated. Simultaneously Prokofyev [6] found yet a third direction for this reaction; in a study of the reaction between diacetyl and dichloroacetyldiketopiperazines with aminopyrimidine in an aqueous medium, symmetrical bis-2,5-pyrimidylpiperazine amidine was isolated. The reaction was accompanied by formation of acetic acid.

Thus, research on the acetyl derivatives of diketopiperazine revealed not only the nature of the final products of their reactions with amines, but also the mechanism of the reaction itself. In all these cases diacetyldiketopiperazine reacted symmetrically.

From our studies of the reactions of diacetyldiketopiperazine it is possible to indicate a number of directions which depend not only on the structure of the substance used, but on the reaction conditions (medium, temperature). Three types of diacetyldiketopiperazine reactions are recognized. The first type is the formation of exoacyl amidines (of glycine, tyrosine, benzylamine). The reaction proceeds irrespective of the presence of any particular acyl group (sulfotoluene, sulfobenzyl, phthalylglycyl, N-chloroacetyl, N-acetyl). The second type is the Bergmann transformation which leads to 1) formation of diketopiperazine and an acetylamino acid, 2) decomposition of diacetyldiketopiperazine to form an N,N'-acetyl dipeptide, 3) formation of an amidine with the removal of an acetyl group (observed by Brunner). The third reaction type includes the formation of monoacetyldiketopiperazine, described in the present paper, which occurs in two cases: 1) by the action of amines on diacetyldiketopiperazine in certain conditions, 2) by the action of diketopiperazine on diacetyldiketopiperazine (on heating in alcohol).

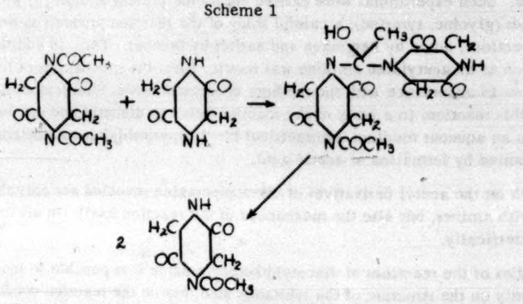
In the great majority of cases these reactions proceed at room temperature in a variety of solvents. However, sometimes it is possible to detect external physical conditions which direct the reaction. For example, when benzylamine reacts with diacetyldiketopiperazine with the reaction mixture cooled by carbon dioxide, an amidine is formed. If the reaction is carried out at room temperature in benzene, chloroform, alcohol, or ether, monoacetyldiketopiperazine and the acetyl dipeptide ester are formed. The reaction between diacetyldiketopiperazine and diaminopyrimidine proceeds at room temperature, and is accompanied by evolution of heat and an almost quantitative amidine yield with acetic acid split off. Thus the direction of this reaction depends on the most varied conditions. The most interesting is the formation of exoacyl amidines by regrouping. The preparation of monoacyl diketopiperazine derivatives is not described in the literature. The formation of monoacetyldiketopiperazine in our experiments is easily explained by a Bergmann regrouping which proceeds asymmetrically. The existence of the monoacetyldiketopiperazine was proved by its conversion into diacetyldiketopiperazine by the action of acetic anhydride, and its ease of decomposition by the action of acids or alkalies into the N-acetyl dipeptide ester.

The mechanism of the action of amines and amino acids on diacetyldiketopiperazine was discovered in a series of our researches. It is also confirmed by Brunner's work, who was the first to show the addition of the amino group at the amide carbonyl with the formation of an amidine, and the subsequent isomerization of the endoacyl amidines into exoacyl amidines. However, the formation both of an acetylated secondary amine, and of monoacetyldiketopiperazine by the action of diacetyldiketopiperazine on diketopiperazine shows that the addition both of amines and of diketopiperazine may take place at the carbonyl group of the endoacetyl, and acetyl amines may be formed without preliminary isomerization to exoacyl amidines.

In previous papers [5] it was shown that the reaction of diacetyldiketopiperazine with glycine esters (methyl and ethyl) produces a substance which, according to our earlier views, was the carboxylic amidine of glycine (with free carboxyl groups). Both with the use of the methyl and of the ethyl ester of glycine the composition of the substance formed was the same. This compound, which had not been described previously, was identified by analysis and study of its behavior on alcoholysis and esterification. However, the empirical formula of this compound is the same as that of monoacetyldiketopiperazine. The melting point and other properties of monoacetyldiketopiperazine, studied by us later, also proved identical with those previously reported for the carboxylic amidine.

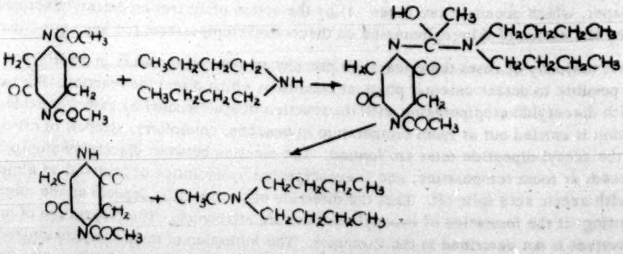
There are no methods available for the synthesis of monoacetyldiketopiperazine. Our attemps to prepare it by heating diketopiperazine with 10 times it amount of glacial acetic acid for 3 hours, with 1 and with 2 moles of acetic anhydride in 10 moles of glacial acetic acid for 11 hours and 3 days respectively, were not successful. It was observed that monoacetyldiketopiperazine is formed by the recrystallization of a mixture of diacetyldiketopiperazine and diketopiperazine from alcohol, and we assumed that these substances react in alcohol. The reaction takes place at the carbonyl in the acetyl group of diacetyldiketopiperazine and the imino nitrogen of diketopiperazine. The exoamidine formed decomposes with the formation of monoacetyldiketopiperazine according to the scheme:

Scheme 1



This scheme applies both to the Brunner reaction and to our experiments on the reaction between diacetyldiketopiperazine and a secondary amine, dibutylamine. In the latter case a regrouping of the acetyl group from the endo to the exo position is impossible, and therefore the formation of dibutylacetamide could take place direct at the exocarbonyl of the acetyl group in diacetyldiketopiperazine, as in the case of diketopiperazine.

Scheme 2



EXPERIMENTAL

I. Reactions of diacetyldiketopiperazine which proceed with the formation of monoacetyldiketopiperazine

1. With glycine ethyl ester. 2.1 g of glycine ethyl ester in 60 ml of anhydrous ether was added to 2.0 g diacetyldiketopiperazine and the mixture shaken mechanically for several hours. The precipitate was filtered off, washed with ether, and treated with acetone in the cold. The small undissolved portion of the precipitate was diketopiperazine. The acetone filtrate after evaporation under vacuum yielded monoacetyldiketopiperazine; m.p. 180°.

Found %: N 17.92. $C_6H_8O_3N_2$. Calculated %: N 17.95.

The ether mother liquor yielded aceturic ester; m.p. 48°. Literature data: m.p. 48° [7].

The reaction with glycine methyl ester is analogous. Monoacetyldiketopiperazine is also formed if the reaction is carried out in benzene.

2. With propylamine. 1.64 g (2 moles) of propylamine was added to 1.98 g (1 mole) of diacetyldiketopiperazine in 100 ml of anhydrous ether and the mixture cooled with snow. The mixture was shaken, and a copious precipitate was instantly formed. After 15 minutes the precipitate was filtered off, washed with ether, and treated with methyl acetate in the cold. The filtrate was concentrated under vacuum to a small volume. The substance formed gave a strong anhydride reaction, and proved to be monoacetyldiketopiperazine (m.p. 180°).

Found %: N 18.03. $C_6H_8O_3N_2$. Calculated %: N 17.95.

The ether filtrate was concentrated under vacuum. The oily residue was distilled, and the 223-225° fraction, which was acetylpropylamine, was collected. Literature data: b.p. 222-225° [8].

3. With aniline. a) A mixture of 2 g (1 mole) of diacetyldiketopiperazine, 100 ml of anhydrous ether, and 1.88 g (2 moles) of aniline was stirred mechanically for 3 days. The precipitate was filtered off, washed with ether, and treated with chloroform in the cold; the filtrate was evaporated under vacuum, and the precipitate formed was recrystallized from alcohol; m.p. 181-182°. Weight 1.5 g. The substance gave the anhydride reaction in the cold, and proved to be monoacetyldiketopiperazine. Total nitrogen content was 17.93%. Acetanilide, m.p. 114°, was isolated from the ether filtrate. Literature data: m.p. 115° [9].

b) 5 g (1 mole) of diacetyldiketopiperazine was dissolved with heating in 100 ml of benzene, and 4.7 g (2 moles) of aniline was added to the cooled solution. The solution was left to stand for twenty-four hours, and the precipitate was filtered off and washed with benzene and ether. The monoacetyldiketopiperazine (m.p. 176-178°) melted at 180-181° after recrystallization from alcohol.

Found %: N 18.13. $C_6H_8O_3N_2$. Calculated %: N 17.95.

Concentration of the benzene filtrate under vacuum gave acetanilide; m.p. 115°.

4. With benzylamine. A mixture of 1.8 g (1 mole) of diacetyldiketopiperazine, 90 ml of anhydrous ether, and 2 ml (2 moles) of benzylamine was mechanically stirred for 30 minutes at room temperature. The precipitate was filtered off, washed with ether, and treated with acetone in the cold; monoacetyldiketopiperazine was isolated from the filtrate. Yield 1.4 g (98%).

Found %: C 46.10, 46.24; H 5.09, 5.10; N 18.09. $C_6H_8O_3N_2$. Calculated %: C 46.15; H 5.12; N 17.95.

Acetylbenzylamine was isolated from the ether filtrate; m.p. 60°. Literature data: m.p. 60-61° [10].

Found %: N 9.43. $C_9H_{11}ON$. Calculated %: N 9.39.

With 1 mole of benzylamine the yield of monoacetyldiketopiperazine was 95%.

5. With dibutylamine. A mixture of 2 g (1 mole) of diacetyldiketopiperazine, 50 ml of ether, and 2.6 g (2 moles) of dibutylamine was shaken mechanically at room temperature for 30 minutes. The precipitate was filtered off, washed with ether and recrystallized from anhydrous alcohol. Monoacetyldiketopiperazine was obtained; m.p. 181°. Yield 1.5 g (94%). Total nitrogen 17.89%. The ether filtrate was evaporated under vacuum and the oily residue was distilled, the 244-245° fraction, which was acetyldibutylamine, being collected. Literature data: b.p. 243-245° [10]. The reaction in benzene took a similar course.

The formation of monoacetyldiketopiperazine in this reaction suggests the formation of an intermediate compound at one of the acetyl groups in diketopiperazine (Scheme 2). This Scheme is confirmed by the reaction between diacetyldiketopiperazine and diketopiperazine, when monoacetyldiketopiperazine was again formed.

6. With diketopiperazine. 4 g of diacetyldiketopiperazine (1 mole) and 2.3 g of diketopiperazine (1 mole) in 40 ml of alcohol were boiled together for 3 hours. The precipitate was filtered off, washed with alcohol, and recrystallized from hot alcohol after filtering off the unreacted diketopiperazine. M.p. 181°. Analysis showed it to be monoacetyldiketopiperazine.

7. With β-naphthylamine. A mixture of 2 g of diacetyldiketopiperazine, 2.9 g of β-naphthylamine, and 50 ml of anhydrous ether was stirred mechanically for 3 days at room temperature and then warmed for several hours on the water bath. The precipitate was filtered off, washed repeatedly with ether, and dried in a vacuum; m.p. 179°. The total nitrogen (17.77%) shows the substance to be monoacetyldiketopiperazine. Unreacted β-naphthylamine was removed from the ether filtrate by precipitation with petroleum ether; m.p. 112°; acetyl-β-naphthylamine m.p. 132°. Literature data: m.p. 132° [11].

8. With p-nitroaniline. A mixture of 2 g of diacetyldiketopiperazine, 1.78 g of p-nitroaniline, and 50 ml of anhydrous ether was shaken mechanically for 3 days and then heated for 5 days. There was no reaction, and only the starting substances were isolated.

II. Reactions of diacetyldiketopiperazine which proceed with the formation of acetylglycylglycine ester

1. With benzylamine. 4.3 g of benzylamine was added to 4 g of diacetyldiketopiperazine in 125 ml of alcohol, and the mixture was shaken 3-5 minutes till the precipitate dissolved. After standing for 30 minutes at room temperature the precipitate was filtered off. The product was monoacetyldiketopiperazine; m.p. 180°. The alcoholic filtrate was concentrated under vacuum, and ether was added to the residue. The precipitate formed was filtered off and washed with ether; m.p. 150°. The substance obtained was the ethyl ester of acetylglycylglycine. Mol.wt. 219 (Rast's method). Literature data: m.p. 153° [12].

Found %: N 14.09. $C_8H_{14}O_4N_2$. Calculated %: N 13.86.

The ethyl ester of acetylglycylglycine was converted into acetylglycylglycine by saponification of the ester groups with alkali.

0.0716 g sub.: consumed 3.67 ml 0.1 N NaOH. $C_8H_{14}O_4N_2$. Calculated: 3.52 ml 0.1 N NaOH.

Concentration of the ether filtrate in vacuum followed by addition of ligroine gave acetylbenzylamine: m.p. 60°. Literature data: m.p. 60-61°.

2. With dibutylamine. A mixture of 2 g of diacetyldiketopiperazine, 50 ml of anhydrous ethyl alcohol, and 2.6 g of dibutylamine was shaken for 2-3 minutes till the precipitate dissolved. When the alcoholic solution was concentrated under vacuum a precipitate was formed, which was filtered off and treated with chloroform in the cold. The melting point of the substance obtained from chloroform was 150-151°; mol. wt. 220 (Rast's method). Melting point of the ethyl ester of acetylglycylglycine according to the literature is 153° [12].

III. Reactions of diacetyldiketopiperazine which proceed with the formation of diketopiperazine

1. With hydrazine in alcohol. Upon the addition of 0.8 g (2 moles) of hydrazine to an alcoholic solution containing 2 g (1 mole) of diacetyldiketopiperazine, much heat was evolved and diketopiperazine was precipitated quantitatively. The medium was neutral at the end of the reaction. The weight of the diketopiperazine formed was 1.0 g, the theoretical yield. Acetyl hydrazide was isolated from the alcoholic filtrate by concentration; m.p. 66-67°. Literature data: m.p. 67° [13].

2. With hydrazine in ether. 0.8 g of hydrazine was added to 2 g of diacetyldiketopiperazine in dry ether with vigorous cooling and shaking. The precipitate formed was filtered off after 30 minutes. By its melting point and analytical date the substance was identified as diketopiperazine.

Found %: N 24.38. $C_4H_6N_2O_2$. Calculated %: N 24.56.

Concentration of the filtrate yielded acetyl hydrazide. Thus, diacetyldiketopiperazine reacts with hydrazine both in alcohol and in ether to form diketopiperazine and acetyl hydrazide.

3. Upon fusion with glycine. 1 g of diacetyldiketopiperazine (1 mole) was mixed with 0.76 g (2 moles) of

glycine in a mortar. The mixture was heated in a test tube in a glycerol bath at 125-130° for 30 minutes. The colored reaction mass was treated with hot acetone and then with alcohol. The residue, by its melting point and properties, was diketopiperazine. A small amount of unreacted diacetyldiketopiperazine was isolated from the acetone filtrate. Aceturic acid, m.p. 206°, was isolated from the alcoholic filtrate.

IV. Some reactions of monoacetyldiketopiperazine

1. Hydrolysis in the presence of alkali. 0.5 g of monoacetyldiketopiperazine in 50 ml of anhydrous alcohol was mixed with 1.5 ml of 0.1 N alcoholic alkali, and the mixture stirred mechanically for several hours. The alcoholic solution was concentrated in a vacuum, and the resultant precipitate proved to be the ethyl ester of acetylglycylglycine; m.p. 153°. The melting point of a synthesized sample of acetylglycylglycine ethyl ester was 153°. A mixture gave no melting point depression. Literature data: m.p. 153°.

2. Alcoholysis in the presence of amines. a) Benzylamine. 1.1 g of monoacetyldiketopiperazine, 0.75 ml of benzylamine, and 75 ml of anhydrous alcohol were mechanically shaken for about one hour. The slight precipitate of diketopiperazine was filtered off. Vacuum concentration of the alcoholic solution gave the ethyl ester of acetylglycylglycine; m.p. 151°.

b) Dibutylamine. 1.1 g of dibutylamine was added to 1.3 g of monoacetyldiketopiperazine in 100 ml of anhydrous alcohol. After 2-3 minutes the solution became clear. The alcoholic solution was concentrated in vacuum and the precipitate washed in ether; m.p. 149°. After recrystallization from alcohol, m.p. 152°. A mixture with acetylglycylglycine ethyl ester obtained in the previous experiment gave no melting point depression.

c) Aniline. A mixture of 0.5 g of monoacetyldiketopiperazine, 0.3 g of aniline, and 35 ml of anhydrous ethyl alcohol was stirred for several days. However, there was no reaction, and the original monoacetyldiketopiperazine was isolated.

3. Alcoholysis in the presence of hydrogen chloride. 0.5 g of monoacetyldiketopiperazine (A) in 20 ml of anhydrous alcohol saturated with HCl (titration of 1 ml of the alcohol took 1 ml of 0.1 N NaOH) was heated for about 5 minutes till the precipitate dissolved completely. Upon further heating a new substance was precipitated, the amount of which increased as the heating proceeded. In crystalline form and melting point the substance was identical with diketopiperazine. The amino nitrogen was determined by Sörensen's method after hydrolysis with water and heating on the water bath for 3 and 30 hours. Diketopiperazine (B) was simultaneously hydrolyzed in the same conditions.

Determination of amino nitrogen by Sörensen's method

Heating for 3 hours: (A) 0.2150 g sub.; took 0.45 ml of 0.2 N NaOH (5.86%). (B) 0.2121 g sub.; took 0.15 ml of 0.2 N NaOH (1.98%). Heating for 30 hours: (A) 0.2219 g sub.: took 0.58 ml of 0.2 N NaOH (7.32%). (B) 0.2195 g sub.: took 0.14 ml of 0.2 N NaOH (1.8%).

The alcoholic filtrate was evaporated in vacuum to a small volume, and ether was added. The precipitate was filtered off, washed with ether, and dried; m.p. 182°. The substance gave the ninhydrin and biuret reactions of the dipeptide type. The reaction for halogens was positive. The substance was the hydrochloride of glycylglycine ethyl ester. Literature data: m.p. 182°.

Found %: N 13.99. $C_6H_{13}O_3N_2Cl$. Calculated %: N 14.2.

Therefore the acid hydrolysis of monoacetyldiketopiperazine yields diketopiperazine and the hydrochloride of glycylglycine ethyl ester.

4. Acetylation to diacetyldiketopiperazine. The action of heat on monoacetyldiketopiperazine with 5 times the quantity of acetic anhydride resulted in the formation of diacetyldiketopiperazine. The yield was theoretical. M.p. 102°. Literature data: m.p. 102°. The formation of diacetyldiketopiperazine is a proof, though indirect, of the structure of monoacetyldiketopiperazine. For complete clarification of the structure of monoacetyldiketopiperazine experiments on the action of acids and alkalies on it in alcoholic solutions were carried out. Acid hydrolysis with 0.1 N hydrochloric acid in anhydrous alcohol produced diketopiperazine and the hydrochloride of glycylglycine ethyl ester.

Under the action of alcoholic alkali (1.5 ml of 0.1 NaOH in 50 ml of alcohol) the diketopiperazine ring was opened with the formation of acetylglycylglycine ethyl ester. This esterification in the presence of alkali is a peculiar and interesting phenomenon. Monoacetyldiketopiperazine is decomposed similarly by the action of benzylamine and butylamine in alcohol.

SUMMARY

Another direction – the formation of monoacetyldiketopiperazine – is added to the numerous directions in the reactions between diacetyldiketopiperazine and amine derivatives. Of the most interesting reactions one should be noted, which leads either to splitting off of acetylamine or to the decomposition of diacetyldiketopiperazine by the action of acids and alkalies to form the acetyl dipeptide. The formation of monoacetyldiketopiperazine is in agreement with the properties of some diketopiperazine derivatives. As is known, diketopiperazine and its derivatives have a tendency to a whole series of asymmetric reactions which lead either to asymmetric rupture of the diketopiperazine ring or to unequal activity of the acyl-substituted groups.

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THE ALKALOIDS OF ACONITUM TALASSICUM M.POP.

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The paper on the alkaloids of Aconitum soongoricum [1] already drew attention to the great theoretical and practical interest presented by study of the group of alkaloids of the genus Aconitum.

The roots of Aconitum talassicum M. Pop. (local name, "kara-parpi") have long been used by the peoples of Central Asia as a medical remedy for a number of diseases. They were first collected for chemical investigation in 1937 in the Talas-Alatau mountains (Western Tyan-Shan). In view of the rarity of this plant its collection involved great difficulties. The first batch of plants collected were used by Konovalova and Orekhov [2] (with the participation of S. Yunusov, who gathered the plants) to isolate the total alkaloids, which comprised 1.64% of the dry plant weight. About one-third of the total was resolved by complex methods, and four new alkaloids were isolated. The following empirical and constitutional formulas were established for them:

Talatisine	$C_{20}H_{29}O_3N$ or $C_{19}H_{23}(NCH_3)(OH)_3\,\Gamma_1$,
Talatisamine	$C_{22}H_{35}O_4N$ or $C_{19}H_{24}(NH)(OH)(OCH_3)_3$,
Isotalatisidine	$C_{23}H_{37}O_5N$ or $C_{19}H_{23}(NC_2H_5)(OH)_3(OCH_3)_2$.
Talatisidine	

The above formulas show that the new alkaloids are of the atizine type, that is, they contain fewer substituent groups than the high molecular aconitines, and therefore form a convenient basis for an approach to the hypothetical nucleus of the aconitic alkaloids, $C_{19}H_{28}NH$.

In 1949 a new extensive growing area of the Talassic aconite was discovered in the Kul-say region (the Turkestan range). The relatively simple formulas of the bases contained in this plant, the availability of the raw material, and certain considerations of the variability of alkaloids with conditions of growth [3], led us to return to an investigation of the alkaloids of this plant.

Most of the raw material studied was gathered either in the budding stage, or in the flowering and post-fertilization stages. The alkaloid content during these stages of the plant development was fairly high: 1.01% in the shoots and 1.92% in the roots.

Separation of the alkaloid mixture by use of the different solubilities in organic solvents, and also by fractionation by basicity function, resulted in the isolation of only about 20% (of the total weight) of the crystalline alkaloids. It was observed, however, that further quantities of the bases crystallized out of the solutions after prolonged standing.

On the assumption that the remaining alkaloids are present as esters which may be largely amorphous, the total amount of alkaloids was subjected to saponification. This immediately raised the yield of crystalline bases to 50%, and the acid saponification products contained veratric acid. Both alkalies and acids were used for the saponification; the reaction products and the yields of crystalline alkaloids were identical in both cases.

The alkaloid present in greatest amount has m.p. 145-146° and does not rotate the plane of polarization. A mixture with the talatisamine isolated by Konovalova and Orekhov showed no melting point depression. Detailed study of this alkaloid showed that its formulas (empirical and constitutional) do not agree with the findings of these authors.

The results of elementary analysis, iodine determination in the hydriodide, and determination of molecular weight by titration, carried out again, corresponded most closely to the formula $C_{24}H_{39}O_5N$ (instead of $C_{22}H_{35}O_4N$).

According to Konovalova and Orekhov, talatizamine contains, in addition to three methoxyl groups, secondary nitrogen and one hydroxyl group. We showed that talatisamine forms a methiodide with methyl iodide, and splits off acetaldehyde on oxidation with permanganate. These reactions show that the nitrogen in the alkaloid is tertiary and is joined to an ethyl radical. The talatisamine molecule, in fact, contains 3 methoxyl groups and 2 active hydrogen atoms, but both the latter belong to hydroxyl groups, as talatisamine forms both a mono and a diacetyl derivative, both with very definite basic properties.

Therefore the constitutional formula of talatisamine may be written as follows:

$$C_{19}H_{23}(NC_2H_5)(OH)_2(OCH_3)_3.$$

The second alkaloid, with m.p. 246-247° an[illegible]$\alpha]_D$ + 36.5°, which contains one double bond and no methoxyl groups, is apparently talatisine. The elementary analysis data are in good agreement with the empirical formula $C_{20}H_{29}O_3N$ which was proposed by Konovalova and Orekhov [2].

EXPERIMENTAL

22.9 kg of the dried and powdered plant material (leaves and stems) was wetted with 10% ammonia solution, loaded into a percolator, and exhaustively extracted with dichloroethane (6 times). The dichloroethane solution was shaken first with 10% and then with 5% sulfuric acid till the alkaloids were completely extracted. The previously filtered solution was made alkaline with a concentrated solution of ammonia in the cold; the alkaloid mixture was precipitated as a viscous mass which was separated from the solution by decantation. The ammoniacal mother liquor was saturated with salt and repeatedly extracted with chloroform. The chloroform extract was concentrated to a small volume and poured into a basin. After complete evaporation of the solvent 51.0 g of a dark brown amorphous mass remained.

a) Treatment of the sparingly soluble alkaloids. 180 g of the pale brown, not quite dry mass was dissolved in 460 ml of 10% sulfuric acid, and the solution was heated under a reflux condenser on a boiling water bath for 5 hours. The acid solution was cooled and shaken several times with ether (ether solution A), filtered to remove resins and slime, and made alkaline with ammonia. The precipitated alkaloids were extracted with chloroform. The chloroform solution was evaporated to a small volume. The resinous mass, after complete removal of the solvent in a vacuum, was triturated with methyl alcohol; a white finely crystalline precipitate of talatisamine was formed (71.2 g), m.p. 140-142°. The methanol liquor was evaporated to dryness and, after the addition of a few milliliters of water, was treated with ligroine, ether, and chloroform. The solutions were evaporated to a small volume and allowed to stand, when an additional amount of talatisamine crystals was formed: 16.0 g from the ligroine solution, 2.9 g from ether, and 2.0 g from chloroform. The total yield of talatisamine was thus 92.1 g. The ether solution A on evaporation deposited white, easily sublimed needles, m.p. 177-179°. These were easily soluble in ether, alcohol, acetone, alkalies, ammonia, and insoluble in water or acids. When recrystallized from dilute alcohol the needles melted at 180-181°. The analytical results showed convincingly that they were veratric acid, $C_6H_3(OCH_3)_2COOH$.

Found %: C 58.97, 59.10; H 5.55, 5.78; OCH_3 33.11, 33.50; equiv. 180.14, 179.36. $C_9H_{10}O_4$. Calculated %: C 59.33; H 5.47; $2OCH_3$ 34.07; equiv. 182.17.

b) Treatment of the alkaloids extracted from the mother liquor. 51.0 g of the mixture of bases was dissolved in 200 ml of 10% sulfuric acid. The filtered solution was separated into 5 fractions according to basicity strength by consecutive precipitation with calculated amounts of ammonia. The final mother liquor was exhaustively extracted with chloroform. The chloroform solution was evaporated to dryness in a vacuum (6th fraction). Each fraction, consisting of a colored amorphous mass, was dissolved in methyl alcohol. Upon standing, the 1st fraction deposited 1.30 g of crystals with m.p. 249-253° (substance was not investigated); 0.66 g of a mixture of alkaloids (m.p. 210-225°) crystallized from the 3rd fraction; the 4th fraction deposited 1.07 g of talatisine, m.p. 245-246°; the 5th fraction deposited 0.67 g of talatisamine, m.p. 144-145°; the 2nd fraction did not yield any crystals.

The alcoholic mother liquors from the 3rd and 4th fractions were combined and partially evaporated to yield a further 2.1 g of talatisamine, m.p. 143-145°, and also 8.8 g of a mixture of talatisine and talatisamine (m.p. 140-180°). It proved possible to separate this mixture by means of 30 ml of cold benzene: the insoluble portion of the mixture (3.0 g) was pure talatisine; the benzene solution, after evaporation to a small volume, deposited 5.2 g of talatisamine.

The alcoholic mother liquors (after separation of the crystals) and the non-crystallizing alcoholic solutions of the 2nd and 6th fractions were combined and saponified by 10% alcoholic KOH solutions for 5 hours. A methanol solution of the saponified alkaloids was evaporated (if possible to remove the alcohol completely) and treated first with ligroine and then with ether.

The ligroine extract was exhaustively extracted with 10% sulfuric acid. The acid solution was made alkaline with 25% ammonia solution, and the alkaloids were consecutively extracted with gasoline and ether. When the ligroine solution was concentrated, 2.5 g of talatisamine crystallized out, and the ether solution yielded 0.28 g of a mixture of alkaloids (m.p. 210-220°).

An ether extract of the saponified alkaloids yielded 0.5 g of talatisamine on evaporation. The residue, after saponification with the alkaloids which did not dissolve in ether and ligroine, was dissolved in sulfuric acid. The acid solution was filtered out, made alkaline with ammonia, and the alkaloids again extracted with ether at the moment of separation. Concentration of the ether solution yielded 0.45 g of a mixture of alkaloids (m.p. 210-225°).

Thus, the mother liquor yielded 10.97 g of talatisamine, 4.07 g of talatisine, and 1.39 g of mixed alkaloids. In the aggregate, 231.0 g of the mixture gave 103.07 g of talatisamine, 4.07 g of talatisine, and 2.69 g of a mixture of alkaloids which was not investigated. The total yield of the crystalline portion relative to the whole mass was 47.6%.

In the same way a total amount of 1250 g of alkaloids was extracted from 65 kg of roots, and separation gave 498 g of talatisamine, 21.7 g of talatisine, and 12.3 g of an unresolved crystalline mixture of alkaloids (m.p. 210-225°).

Talatisamine. The crude talatisamine was crystallized several times from methanol until crystals with constant m.p. 145-146° were obtained.

4.720, 3.251 mg sub.: 11.767, 8.136 mg CO_2; 3.968, 2.761 mg H_2O. 7.125, 5.675 mg sub.: 0.225, 0.186 ml N_2 (22°, 734 mm). 10.530, 8.988 mg sub.: 8.81, 7.63 ml 0.05 N. $Na_2S_2O_3$ (for OCH_3). 3.154 mg sub.: 3.30 ml 0.02 N $Na_2S_2O_3$ (for NC_2H_5). 0.9909, 1.0036 g sub.: 23.536, 23.785 ml 0.1 N H_2SO_4 (methyl red). Found %: C 68.04, 68.29; H 9.41, 9.50; N 3.53, 3.66; OCH_3 21.64, 21.95; NC_2H_5 15.01; equiv. 421.11. $C_{24}H_{39}O_5N$. Calculated %: C 68.37; H 9.33; N 3.32; $3OCH_3$ 22.08; NC_2H_5 10.21; equiv. 421.56.

Talatisamine hydrobromide was prepared by the addition of hydrobromic acid to the base till an acid reaction was obtained. The liquid was left in an open basin for several days, when crystals were formed which had m.p. 78-80° after recrystallization from ethyl acetate. Talatisamine hydrobromide crystallizes with two molecules of water. After drying in a vacuum the melting point of the salt was almost unchanged (80-81°).

Found %: H_2O 7.15. $C_{24}H_{39}O_5N \cdot HBr \cdot 2H_2O$. Calculated %: H_2O 6.70.

Talatisamine hydriodide. 3 g of the base was dissolved in 30 ml of acetone with gentle heating. The clear solution was cooled, and concentrated hydriodic acid was added (till weakly acid to litmus), followed by the careful addition of 25 ml of ether. After several days crystals of the hydriodide were obtained in the form of warty nodules, m.p. 66-68°. Yield 3.8 g. Talatisamine hydriodide is easily soluble in water and alcohol, less so in acetone. After recrystallization from a mixture of alcohol and acetone (1 : 1) the salt was precipitated in the form of colorless four-sided prisms with 3 molecules of water of crystallization; m.p. 67.5-68.5°.

0.6010 g sub. in 10.0 ml water: $\underline{1}$ 10.0 $\alpha_D -0.77°$, $[\alpha]_D -12.8°$.

1.6962 g sub.: 0.1481 g H_2O. 0.2034, 0.1911 g sub.: 3.30, 3.16 ml 0.1 N $AgNO_3$. Found %: H_2O 8.73; I 20.57, 20.96. $C_{24}H_{39}O_5N \cdot HI \cdot 3H_2O$. Calculated %: H_2O 8.95; I 21.03.

The anhydrous salt has no sharp melting point: it shrinks at 130° and then froths.

0.5472 g sub. in 10 ml water: $\underline{1}$ 10.0, $\alpha_D -0.77°$, $[\alpha]_D -14.8°$.

0.2520, 0.2532 g sub.: 4.64, 4.61 ml 0.1 N $AgNO_3$. Found %: I 23.39, 23.12. $C_{24}H_{39}O_5N \cdot HI$. Calculated %: I 23.09.

Monoacetyltalatisamine. A mixture of 1 g of the base and 2 ml of acetic anhydride was placed in a flask with a ground glass stopper and left to stand for 13 days till a viscous homogeneous mass was formed. A small amount of water was added to this mass, the solution was made alkaline with ammonia, and the precipitated bas was extracted with ether. The oil obtained by evaporation of the ether solution crystallized after standing. After recrystallization from methanol the monoacetyltalatisamine had m.p. 97-98°. Saponification of the acetyl derivative gave the original talatisamine.

Diacetyltalatisamine. A mixture of 1 g of the base and 2 ml of acetyl chloride was left in a closed vessel till a homogeneous solution was formed. After 12 days the excess acetyl chloride was driven off from the reaction mass (first on the water bath, then under vacuum). A small amount of water was added to the residue, the solution was made alkaline with ammonia, and the precipitated base was exhaustively extracted with ether. The ether extract was concentrated to a small volume and poured into a basin. After complete volatillization of the solvent an oil remained, which crystallized after standing. The diacetyltalatisamine was recrystallized from methyl alcohol and had m.p. 127-129°. A sample mixed with monoacetyltalatisamine showed depression of melting point.

0.5540 g sub. in 10.0 ml methyl alcohol: $\underline{1}$ 10.0, $\alpha_D - 0.25°$, $[\alpha]_D - 5.05°$.

0.5136, 0.4945 g sub.: 10.1, 9.75 ml 0.1 N HCl (methyl red). Found %: equiv. 508.5, 507.2. $C_{28}H_{43}O_7N$. Calculated: equiv. 505.63.

Saponification of diacetyltalatisamine. Alcoholic alkali solution was added to weighed samples of diacetyltalatisamine. The mixture was boiled on the water bath under a reflux condenser and the excess alkali was titrated with acid.

0.3182, 0.3016 g sub.: 11.86 11.86 ml 1 N KOH. Found %: CH_3CO 11.30, 11.90. $C_{24}H_{37}N(CH_3COO)_2$. Calculated %: CH_3CO 11.60.

After removal of the solvent on the water bath and then under vacuum, alkali was added to the solution, and the base was extracted with ether. Crystals were deposited from the ether solution after evaporation, and after recrystallization from methanol the crystals melted at 144-145°. No melting point depression was given by a sample mixed with talatisamine.

Talatisamine methiodide. A mixture of 4 g of the base and 10 ml of methyl iodide was sealed in an ampoule and heated on a boiling water bath for 6 hours. The ampoule was opened and the crystals formed were separated off and washed with ether, m.p. 220-221°. Yield 1.35 g. Crystals of the original talatisamine were deposited from the mother liquor after evaporation. The melting point of the methiodide did not change after recrystallization from methyl alcohol with the addition of ether.

Oxidation of talatisamine. 0.5 g of potassium permanganate dissolved in 10 ml of water was added to a solution of 1 g of the base in 10 ml of N sulfuric acid cooled by ice, dropwise with stirring during 1 hour. The reaction mixture was filtered, the precipitate was washed with 6 ml of water, and the filtrate was distilled into a cooled receiver. 30 ml of hot 1% aqueous dimedon solution was added to the distillate, and the mixture was then heated for 10 minutes on the water bath. After 1 hour a bulky crystalline precipitate (0.21 g) was deposited from the cooled solution, m.p. 134-136°. After recrystallization from ligroine the crystals had m.p. 136-138°. A mixture of the condensation product of acetaldehyde with dimedon with m.p. 138-140°, melted at 138-139°.

Talatisine. Talatisine was recrystallized from methanol. The result was a colorless crystalline substance, m.p. 246-247°. Upon catalytic hydrogenation over platinum oxide the alkaloid absorbed a quantity of hydrogen which approximately corresponded to the presence of one double bond.

0.1700 g sub. in 10 ml anhydrous alcohol: $\underline{1}$ 10.0, $\alpha_D + 0.62°$, $[\alpha]_D + 36.5°$.

Found %: C 72.30, 72.05; H 8.72, 8.82; N 4.22, 4.47. $C_{20}H_{29}O_3N$. Calculated %: C 72.50; H 8.76; N 4.23.

SUMMARY

1. The alkaloids talatisamine and talatisine were isolated from Aconitum talassicum M. Pop. Veratric acid was found in the saponification products of the alkaloid mixture.

2. The following corrected constitutional formula is given for talatisamine as the result of functional group determinations and the preparation of certain new derivatives:

$$C_{19}H_{23}(NC_2H_5)(OH)_2(OCH_3)_3.$$

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THE ACONITE ALKALOIDS

VI. ELATINE

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The previous paper [1] gave the results of a chemical investigation of a Delphinium species – Delphinium elatum (tall larkspur) which grows in the Altay region. In addition to a new crystalline alkaloid, named eldeline, we isolated another crystalline base, provisionally designated as Base No. 2. Its peculiarity is the solubility of its sulfate in chloroform, which made it possible to isolate it in the pure state for the first time. Base No. 2 is separated from the ether mother-liquors after removal of eldeline, and its content does not exceed 0.03-0.04% of the dry plant weight. The alkaloid, recrystallized from ethyl or methyl alcohol, melts at 222-225°, specific rotation + 3.4° (in chloroform), forms an amorphous hydrochloride, m.p. 180-210° (decomp.), and a crystalline perchlorate, m.p. 175-200°. From elementary analysis data for the base and the perchlorate, the composition of the base was established as $C_{38}H_{50}O_{10}N_2$. As the newly isolated base differs in its properties from the known alkaloids, we gave it the name of elatine.

Saponification of elatine with alcoholic caustic soda solution gives a crystalline amino alcohol and a crystalline nitrogen-containing acid, which were named elatidine and elatinic acid respectively.

Elatidine, recrystallized from aqueous acetone, melts at 172-174°, and forms a crystalline hydrobromide with m.p. 206.5-207.5° (decomp.). The action of methyl iodide, as in the case of the amino alcohol delartine [2] forms the hydriodide, m.p. 197-197.5°. Acetylation of elatidine gave a monoacetyl derivative isolated as the hydrochloride, m.p. 205-208° (decomp.). On the basis of elementary analysis of the base, its hydrobromide, and the monoacetyl derivative, elatine was assigned the composition $C_{26}H_{41}O_7N$.

Elatinic acid melts at 154-155.5°, and is a dibasic acid, the equivalent of which is 125. Its composition, by elementary analysis, was established as $C_{12}H_{13}O_5N$. Thus, the alkaline hydrolysis of elatine may be represented by:

$$\underset{\text{elatine}}{C_{38}H_{50}O_{10}N_2} + 2H_2O \longrightarrow \underset{\text{elatidine}}{C_{26}H_{41}O_7N} + \underset{\text{elatinic acid}}{C_{12}H_{13}O_5N}.$$

When elatinic acid is heated with 10% hydrochloric acid, two crystalline acids are formed: one of these after sublimation and recrystallization from water melted at 144-145° and was anthranilic acid. The second acid, after recrystallization from a mixture of alcohol and acetone, melted at 183-185° (decomp.), and was sparingly soluble in ether and easily in water. In its composition and properties of the decomposition products elatinic acid greatly resembles delartinic acid, which was isolated after the saponification of delartine [2]; their identity is quite probable, and this may be proved by direct comparison.

EXPERIMENTAL

Isolation of elatine

The ether mother liquor after separation of eldeline [1] was treated with 10% sulfuric acid. The resultant sulfuric acid solution was repeatedly extracted with chloroform, when the elatine passed into chloroform solution. After removal of the chloroform under vacuum a syrupy substance remained, which was dissolved in a small amount of 10% sulfuric acid. The acid solution was washed with ether, and then carefully, with cooling, made alkaline with 25% ammonia; elatine crystallized out in the form of a yellowish-grey powder. After 2 recrystallizations from ethyl alcohol (1 : 10) in the presence of carbon, elatine separated out as colorless needles, m.p. 222-225° in a yield of 0.03-0.04% on the dry plant weight.

0.1036 g sub. (3 ml chloroform, $\underline{1}$ 0.5); $[\alpha]_D + 3.4°$.

4.539 mg sub.: 10.922 mg CO_2; 3.023 mg H_2O. 3.383 mg sub.: 8.149 mg CO_2; 2.200 mg H_2O. 6.272 mg sub.: 0.244 ml N_2 (22.5°, 733.5 mm). 6.800 mg sub.: 0.259 ml N_2 (25°, 733.0 mm). 0.1035 g sub.: 1.5 ml 0.1 N HCl (methyl red). Found %: C 65.67, 65.73; H 7.45, 7.27; N 4.34, 4.20. M 690. $C_{38}H_{50}O_{10}N_2$. Calculated %: C 65.70; H 7.20; N 4.03. M 694.

The hydrochloride was formed upon acidification of a solution of elatine in anhydrous alcohol with alcoholic hydrochloric acid; it was isolated as an amorphous powder by the addition of anhydrous ether, and it decomposes at 180-210°.

The perchlorate was formed by mixing aqueous solutions of elatine hydrochloride and sodium perchlorate. After recrystallization from aqueous alcohol, with slow cooling, the salt with an indistinct m.p. 175-200° (decomp.) crystallized out.

3.573 mg sub.: 7.475 mg CO_2; 2303 mg H_2O. 3.300 mg sub.: 6.842 mg CO_2; 2.074 mg H_2O. 7.051 mg sub.: 0.199 ml N_2 (23°, 735 mm). 7.165 mg sub.: 1.505 mg AgCl. 7.161 mg sub.: 1.462 mg AgCl. Found %: C 57.09, 56.58; H 7.21, 7.03; N 3.15, 3.25; Cl 5.12, 5.05. $C_{38}H_{50}O_{10}N_2 \cdot HClO_4$. Calculated %: C 57.42; H 6.3; N 3.52; Cl 4.47.

Elatidine

A mixture of 3 g of elatine, 10 ml of 96% alcohol, and 12 ml of 1 N NaOH was heated on the water bath under a reflux condenser for 3 hours, after which the alcohol was evaporated off. Several milliliters of water was added to the residue, and elatidine then crystallized out, the yield being 1.9 g, m.p. 160-162°. It crystallized in the form of needles after being dissolved in 1% hydrochloric acid followed by treatment with charcoal and careful neutralization of the acid solution with 2% ammonia. After recrystallization from acetone the m.p. was 172-174°.

3.855 mg sub.: 9.204 mg CO_2; 2.970 mg H_2O. 3.492 mg sub.: 8.359 mg CO_2; 2.762 mg H_2O. 8.805 mg sub.: 0.242 ml N_2 (26.5°, 730 mm). 8.610 mg sub.: 0.240 ml N_2 (26.5°, 730 mm). 4.274 mg sub.: 10.73 ml 0.02 N $Na_2S_2O_3$. 4.744 mg sub.: 12.00 ml 0.02 N $Na_2S_2O_3$. Found %: C 65.15, 65.32; H 8.62, 8.85; N 3.01, 3.05; OCH_3 25.97, 26.15. $C_{26}H_{41}O_7N$. Calculated %: C 65.10; H 8.56; N 2.92; $4OCH_3$ 25.88.

The hydrobromide crystallized after the addition of concentrated hydrobromic acid to a solution of elatidine in acetone. After recrystallization from acetone (1 : 3) and drying at 100°, m.p. was 206.5-207.5°.

3.450 ml sub.: 6.933 mg CO_2; 2.260 mg H_2O. 3.539 mg sub.: 7.088 mg CO_2; 2.371 mg H_2O. 8.420 mg sub.: 0.206 ml N_2 (27°, 730 mm). Found %: C 54.84, 54.66; H 7.33, 7.49; N 2.67. $C_{26}H_{41}O_7N \cdot HBr \cdot 0.5H_2O$. Calculated %: C 54.83; H 7.55; N 2.46.

The hydriodide. 0.5 g of elatidine in methyl alcohol solution was heated with methyl iodide in a sealed tube at 70-75° for 3 hours. After evaporation of the solvent the residue was repeatedly treated with ether and then dissolved in acetone, from which it was crystallized out by the addition of anhydrous ether. After being dried to constant weight it melted at 197-198.5°. When a few drops of 5% ammonia were added to an aqueous solution of the substance, a base crystallized out which was identical with the original elatidine.

Acetylation of elatidine. A mixture of 0.5 g of elatidine and 3 ml of acetyl chloride was heated in a sealed tube at 50-60° for 16 hours. After the removal of excess acetyl chloride the residue was treated with a few milliliters of water, made alkaline with 25% ammonia, and extracted with ether. After evaporation of the solvent the remaining oily base was dissolved in acetone and converted into the hydrochloride by the addition of alcoholic hydrochloric acid. After recrystallization from alcohol-acetone mixture and the addition of anhydrous ether, acetylelatidine hydrochloride separated out, m.p. 205-208° (decomp.).

3.727 mg sub.: 8.238 mg CO_2; 2.779 mg H_2O. 3.900 mg sub.: 8.580 mg CO_2; 2.800 mg H_2O. 9.957 mg sub.: 0.236 mg N_2 (22°, 733 mm). 10.390 mg sub.: 0.258 ml N_2 (20.5°, 728 mm). Found %: C 60.32, 60.04; H 8.34, 8.03; N 2.65, 2.76. $C_{28}H_{43}O_8N \cdot HCl$. Calculated %: C 60.26; H 7.71; N 2.51.

Elatinic acid

Acidification of the alkaline mother liquor, after isolation of elatidine, with sulfuric acid resulted in the separation of elatinic acid in the form of an oil which was converted into a pale orange powder by rubbing. This was dissolved in 1 N NaOH and then carefully acidified with 1 N hydrochloric acid; an oil was first formed, which was filtered off; the filtrate yielded a colorless crystalline acid, m.p. 154-155°.

3.133 mg sub.: 6.587 mg CO_2; 1.359 mg H_2O. 1.308 mg sub.: 2.756 mg CO_2; 0.669 mg H_2O. 7.035 mg sub.: 0.326 ml N_2 (22.5°, 733.5 mm). 7.010 mg sub.: 0.341 ml N_2 (25°, 733.0 mm). Found %: C 57.38, 57.39; H 5.49, 5.72; N 5.17, 5.37. $C_{12}H_{13}O_5N$. Calculated %: C 57.37; H 5.17; N 5.4.

Saponification of elatinic acid. a) 0.5 g of elatinic acid was boiled 1.5 hours with 3 ml of 10% hydrochloric acid. After dilution with an equal volume of water the solution was repeatedly extracted with ether, which was evaporated off to give 0.35 g of a crystalline acid. The acid was purified by vacuum sublimation at 120-125° followed by recrystallization from water, m.p. 141-142°. A sample mixed with anthranilic acid gave no depression of melting point.

b) The aqueous acid mother liquor, from which the anthranilic acid was extracted with ether, was evaporated under vacuum. The residue was a dark crystalline acid, in a yield of 0.15 g, which was purified by solution in a mixture of alcohol and acetone, from which it was crystallized by the addition of ether, m.p. 183-185° (without decomp.).

SUMMARY

1. From Delphinium elatum (tall larkspur) a new crystalline alkaloid with the composition $C_{38}H_{50}O_{10}N_2$, named elatine, has been isolated.

2. Elatine was found to be an ester, the alkaline hydrolysis of which gave a crystalline amino alcohol of the composition $C_{26}H_{41}O_7N$, named elatidine, and a crystalline acid of the composition $C_{12}H_{13}O_5N$, named elatinic acid.

3. The acid hydrolysis of elatinic acid gave two crystalline acids, one of which was anthranilic acid.

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INVESTIGATION OF THE ALKALOIDS FROM THE PLANT LEONTICE EWERSMANNII BGE.

II. THE DECOMPOSITION PRODUCTS OF TASPINE

T. F. Platonova and A. D. Kuzovkov

The alkaloid taspine was isolated from the shoot portions of the Leontica plant. On the basis of analytical data and functional group determinations, it was assigned the formula $C_{20}H_{19}O_6N$, or

$$C_{14}H_5(OCH_3)_2(CH_2O_2)(COO)N(CH_3)_2 \text{ [1]}.$$

We continued our investigation of this alkaloid with an attempt to determine the nature of its carbon skeleton. Distillation of taspine with zinc dust gave fluorene. Fusion of taspine with solid caustic potash gave a crystalline substance with the composition $C_{12}H_{10}O_4$ (m.p. 217.5-218.5°) with four phenolic hydroxyls, as shown by its elementary composition, hydroxyl group determination, the formation of a tetraacetyl derivative (m.p. 87-88.5°) and of products of methylation by means of diazomethane: $C_{12}H_6(OCH_3)_4$ (m.p. 100.5-101.5°) and

$$C_{12}H_6(OH)(OCH_3)_3 \text{ (m.p. 127.5-128.5°)}.$$

Oxidation of the substance $C_{12}H_{10}O_4$ gave 2,3-dihydroxybenzoic acid, and distillation with zinc dust gave diphenyl.

Therefore the substance $C_{12}H_{10}O_4$ is 2,3,x',y'-tetrahydroxydiphenyl. Our tetrahydroxydiphenyl isomer differs from those described in the literature. The formation of a tetrahydroxydiphenyl isomer and of fluorene leads to the supposition, which obviously requires further confirmation, that taspine may be regarded as a diphenyl derivative.

In our first communication on taspine the view was put forward that the amino group in the molecule of this alkaloid is in an open chain. This was confirmed as follows. Boiling of taspine with hydrobromic acid resulted in saponification of the lactone group, and of methoxyl and methylenedihydroxy groups, and an amino acid named taspininic acid was formed. The hydrobromide of this acid melts at 298° and has the composition $C_{17}H_{17}O_7N \cdot HBr$.

The oxidation of taspininic acid by potassium permanganate in sulfuric acid solution gave β-dimethylaminopropionic acid (m.p. 143-144°, hygroscopic), its hydrochloride (m.p. 186-188°), reineckate (m.p. 164-175°), ethyl ester (b.p. 62-64° at 15 mm), ethyl ester hydrochloride (m.p. 143-145°) and the methiodide of the ethyl ester (m.p. 175°). The formation of β-dimethylaminopropionic acid indicates the presence in taspininic acid, and possibly also in taspine, of the side chain $CH_2CH_2 \cdot N(CH_3)_2$, and may perhaps be attributed to the fact that oxidation results in the destruction of aromatic nuclei (containing a large number of phenolic groups) and the formation of the carboxyl group of β-dimethylaminopropionic acid at the carbon atom of the aromatic ring which is linked to the side chain.

EXPERIMENTAL

Distillation of taspine with zinc dust. 5 g of taspine was distilled by the well-known method with 50 g of zinc dust in a stream of dry hydrogen. Volatile amines were evolved, and were absorbed in 10% hydrochloric acid solution. After cooling, the solid and liquid reaction products were extracted with ether. Bases were removed from the ether solution by shaking it with 2% hydrochloric acid and washing with water. After removal of the ether, 50 ml of alkaline water was added to the residue and the volatile products were distilled in steam. The distillate was twice extracted with ether. The extract, after drying and removal of solvent, gave 0.07 g of a partly crystalline residue from which a colorless crystalline substance was sublimed at low pressure (20 mm) at 100°, the melting point of which after 2-fold recrystallization from alcohol was 108.5-109.5°. A sample mixed with fluorene did not give a melting point depression.

The hydrochloric acid solution of the amines was evaporated almost to dryness. When picric acid was added to the residue, a crystalline picrate was precipitated, m.p. 225-226° (from alcohol).

Found %: C 37.73; H 4.62; N 19.69. $C_9H_{12}O_7N_4$. Calculated %: C 37.51; H 4.19; N 19.44.

Fusion of taspine with solid caustic potash. 4 g of taspine and 16 g of caustic potash were heated together in a round-bottomed flask of 500 ml capacity, in a stream of dry nitrogen till the mixture fused into a homogeneous brown mass. The melt was dissolved in 150 ml of 10% sulfuric acid, the solution was filtered, and repeatedly extracted with ether. After removal of the ether 1.6 g of a crystalline substance was obtained. After 2-fold crystallizations from toluene fine needles were obtained, m.p. 217.5-218.5 g. Yield 0.7 g. The substance was soluble in ether, alcohol, and acetone, sparingly soluble in toluene.

3.511 mg sub.: 8.540 mg CO_2; 1.548 mg H_2O. 4.221 mg sub.: 10.243 mg CO_2; 1.913 mg H_2O. 5.188 mg sub.: 2.50 ml CH_4 (19.5°, 742 mm). 3.900 mg sub.: 1.85 ml CH_4 (19.5°, 742 mm). 0.0102 g sub.; 0.1022 g camphor: Δt 17.3°. Found %: C 66.38, 66.22; H 4.93, 5.07; OH 33.69, 33.16. M 231. $C_{12}H_{10}O_4$. Calculated %: C 66.05; H 4.62; 4OH 31.16. M 218.2.

Methylation of tetrahydroxydiphenyl. 0.75 g of tetrahydroxydiphenyl in 20 ml of ether was mixed with a solution of diazomethane in ether (from 8.5 g of nitrosomethylurea) and left 4 days. For separation of the phenolic and nonphenolic products the oily residue after removal of the ether was dissolved in 5% caustic soda solution and repeatedly extracted with ether.

The substances from the ether extract, after removal of the solvent, were dissolved in benzene and purified by shaking with 5% solution of alkali. After drying of the benzene extract and removal of the solvent, 0.18 g of a crystalline substance was obtained, which, after 2-fold recrystallization from 75% alcohol, melted at 100.5-101.5°.

3.909 mg sub.: 10.071 mg CO_2; 2.369 mg H_2O. 4.177 mg sub.: 10.766 mg CO_2; 2.489 mg H_2O. 3.613 mg sub.: 16.05 ml N $Na_2S_2O_3$. 3.158 mg sub.: 14.00 ml 0.02 N $Na_2S_2O_3$. Found %: C 70.31, 70.34; H 6.78, 6.77; OCH_3 45.31, 45.21. $C_{12}H_6(OCH_3)_4$. Calculated %: C 70.05; H 6.61; 4OCH_3 45.24.

The aqueous alkaline solutions, after acidification and extraction with ether, yielded 0.25 g of a substance which, after 3-fold recrystallization from alcohol, melted at 127.5-128.5°.

3.552 mg sub.: 8.949 mg CO_2; 1.961 mg H_2O. 3.190 mg sub.: 8.040 mg CO_2; 1.770 mg H_2O. 7.583 mg sub.: 26.71 ml 0.02 N $Na_2S_2O_3$. 4.262 mg sub.: 14.92 ml 0.02 N $Na_2S_2O_3$. Found %: C 68.75, 68.78; H 6.18, 6.20; OCH_3 35.93, 35.71. $C_{12}H_6(OH)(OCH_3)_3$. Calculated %: C 69.24; H 6.19; 3OCH_3 35.75.

Acetylation of tetrahydroxydiphenyl. 1.25 g of tetrahydroxydiphenyl and 20 ml of acetyl chloride were boiled under a reflux condenser for 1.5 hours. After removal of the excess acetyl chloride under vacuum, the reaction products (1.6 g) were dissolved in ether and repeatedly washed with 5% caustic soda solution to remove acid and phenolic impurities. Evaporation of the ether solution to a small volume resulted in the precipitation of 1.4 g of colorless needles, m.p. 87-88.5°. The melting point did not alter after crystallization.

4.480 mg sub.: 10.246 mg CO_2; 1.919 mg H_2O; 3.423 mg sub.: 7.830 mg CO_2; 1.483 mg H_2O. Found %: C 62.41, 62.42; H 4.79, 4.84. $C_{12}H_6(OCOCH_3)_4$. Calculated %: C 62.18; H 4.69.

Oxidation of tetraacetyltetrahydroxydiphenyl. 3.4 g of chromic anhydride was added to 1.2 g of tetraacetyltetrahydroxydiphenyl in 10 ml of glacial acetic acid at 70° during 1.5 hours with constant stirring. The reaction mass was diluted with water to 150 ml and extracted 3 times with ether. The residue after removal of the ether was evaporated under vacuum to remove acetic acid, and dissolved in 5% aqueous ammonia. The solution was washed with ether and acidified with 10% sulfuric acid. Extraction with ether gave an acid (0.09 g) which, after sublimation under vacuum at 110-115° and crystallization from water, melted at 200-202°. Repetition of the sublimation and crystallization raised the m.p. to 205-206°. Yield 0.05 g. A sample mixed with 2,3-dihydroxybenzoic acid produced no depression of melting point.

Found %: C 54.81, 54.50; H 4.42, 4.34. $C_7H_6O_4$. Calculated %: C 54.55; H 3.92.

Distillation of tetrahydroxydiphenyl with zinc dust. 1.9 g of tetrahydroxydiphenyl was distilled with 19 g of zinc dust in a stream of dry hydrogen. The reaction products were dissolved in ether, shaken with 2% caustic soda solution to remove acids and phenols, and washed with water. After removal of the ether 0.27 g of resinous crystals remained, which, after sublimation at 100° and 2-fold recrystallization from alcohol, consisted of shiny plates, m.p. 65.5-67°. A sample mixed with diphenyl melted at the same temperature.

Found %: C 93.43; H 6.50. $C_{12}H_{10}$. Calculated %: C 93.46; H 6.53.

Preparation of taspininic acid. 20 g of taspine and 200 ml of hydrobromic acid (d = 1.48) were boiled together for 3 hours till the alkaloid dissolved completely. The reaction product, which crystallized in the form of needles when the reaction mass was cooled, was filtered, washed with acetone, and recrystallized from dilute hydrobromic acid. Yield 23 g, m.p. 298° (decomp.).

3.373 mg sub.: 5.980 mg CO_2; 1.327 mg H_2O. 4.340 mg sub.: 7.729 mg CO_2; 1.778 mg H_2O. 9.601 mg sub.: 0.270 ml N_2 (23°, 735 mm). 5.861 mg sub.: 0.166 ml N_2 (23°, 735 mm). Found %: C 48.38, 48.60; H 4.40, 4.58; N 3.14, 3.16. $C_{17}H_{18}O_7NBr$. Calculated %: C 47.68; H 4.23; N 3.26.

Taspininic acid was isolated in the form of a bulky amorphous precipitate by the neutralization of 23 g of the hydrobromide in 170 ml of water with 5% caustic soda (to a weakly acid reaction to methyl red). The precipitate was washed with water and dried at 100° in vacuum. Yield 19 g. Taspininic acid is insoluble in water, alcohol, or acetone, and dissolves in acids and alkalies.

Oxidation of taspininic acid. 1.9 liters of 3.5% potassium permanganate solution was added to a filtered solution of 19.5 g of taspininic acid in 3.9 liters of 5% H_2SO_4 with vigorous stirring for 6 hours. The addition was stopped when a manganese dioxide precipitate which did not disappear in the course of an hour was formed. The precipitate was filtered off; the transparent slightly yellowish filtrate was evaporated under vacuum to a volume of about 2 liters, made alkaline with 40% caustic soda, and again acidified with hydrochloric acid (1 : 1) against methyl orange, and then evaporated to dryness. The reaction products were extracted 3 times from the residue, which contained large quantities of inorganic salts, by anhydrous alcohol acidified with gaseous HCl. After removal of the alcohol the residue was dissolved in 60 ml of water and shaken with ether to remove acid impurities. The aqueous solution was made alkaline with caustic soda (solution A), and organic bases were extracted with ether. The ether extract was dried with solid caustic potash, and alcoholic HCl was added to give the hydrochloride which, after crystallization from alcohol, was in the form of colorless needles, m.p. 143-145°. Yield 2.4 g.

3.800 mg sub.: 6.469 mg CO_2; 3.020 mg H_2O. 4.359 mg sub.: 7.402 mg CO_2; 3.482 mg H_2O. 6.255 mg sub.: 0.35 ml N_2 (17°, 740 mm). 6.55 mg sub.: 1.88 ml 0.02 N NH_4CNS. 8.122 mg sub.: 2.30 ml 0.02 N NH_4CNS. Found %: C 46.46, 46.34; H 8.89, 8.94; N 6.44; Cl 20.35, 20.08. $C_7H_{15}O_2N \cdot HCl$. Calculated %: C 46.29; H 9.08; N 7.71; Cl 19.52.

The base was obtained from the hydrochloride (2.3 g) in the usual way, b.p. 62-64° (15 mm). Yield 0.82 g.

Methiodide. 0.3 g of methyl iodide was added to 0.3 g of the base, and a violent reaction took place with the formation of a crystalline substance. After recrystallization from alcohol this had m.p. 175°, fine needles, yield 0.46 g.

12.720 mg sub.: 26.40 ml 0.01 N $Na_2S_2O_3$. 7.848 mg sub.: 16.50 ml 0.01 N $Na_2S_2O_3$. Found %: I 43.92, 44.49. $C_7H_{15}O_2N \cdot CH_3I$. Calculated %: I 44.19.

Saponification of the base. 0.1 g of the base was heated for 1 hour with 2 ml of 5% caustic soda solution at 100° in a sealed tube. The solution was cooled, acidified with 20% sulfuric acid, and washed by shaking with ether; the addition of a solution of Reinecke salt gave the crystalline reineckate which, after being washed with water and dried in a vacuum dessicator, melted at 168-174°.

The addition of an aqueous solution of 5 g of Reinecke salt saturated at 60° to solution A after acidification with hydrochloric acid (1 : 1) gave the crystalline reineckate which, after being washed with water and dried in a vacuum desiccator, melted at 164-175°. Yield 5.4 g. A mixture with the reineckate obtained previously after saponification of the base melted at the same temperature.

Preparation of β-dimethylaminopropionic acid. 4.6 g of the reineckate was triturated with 100 ml of 10*a* hydrochloric acid, and the Reinecke acid was extracted by ethyl acetate. The ethyl acetate extract was washed 3 times with 5% hydrochloric acid. The acid extracts were added to the main aqueous hydrochloric acid extract, decolorized by charcoal, and evaporated to dryness under vacuum. The partly crystallized residue was dissolved in 20 ml of anhydrous alcohol and filtered. Ether was added to isolate the crystalline hydrochloride. After three crystallizations from a mixture of alcohol and ether the yield was 0.65 g, fine needles, m.p. 181-182°. The product is easily soluble in water, less so in alcohol, and is insoluble in acetone or ether.

4.660 mg sub.: 6.690 mg CO_2; 3.118 mg H_2O. 4.672 mg sub.: 6.700 mg CO_2; 3.210 mg H_2O. 8.197 mg sub.: 0.608 ml N_2 (22°, 731 mm). 11.240 mg sub.: 3.54 ml 0.02 N NH_4CNS. Found %: C 39.18, 39.13; H 7.49, 7.69; N 8.25; Cl 22.33. $C_5H_{11}O_2N \cdot HCl$. Calculated %: C 39.07; H 7.87; N 9.11; Cl 23.08.

0.5 g of the hydrochloride in 5 ml of water was shaken with moist silver oxide (from 0.66 g $AgNO_3$), the solution was filtered, silver ions were removed by hydrogen sulfide, and the solution was evaporated to dryness under a vacuum; the crystalline extract was twice crystallized from acetone. The yield was 0.2 g of a colorless, highly hygroscopic substance, needles, m.p. 143-144°. A sample mixed with β-dimethylaminopropionic acid melted at the same temperature.

3.468 mg sub.: 6.445 mg CO_2; 2.852 mg H_2O. 5.430 mg sub.: 10.108 mg CO_2; 4.588 mg H_2O. 8.720 mg sub.: 0.890 ml N_2 (19°, 748 mm). 7.849 mg sub.: 6.60 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: C 50.72, 50.80; H 9.20, 9.45; N 11.74, 11.77. $C_5H_{11}O_2N$. Calculated %: C 51.26; H 9.46; N 11.95.

The hydrochloride of the amino acid was prepared by the addition of alcoholic HCl to a solution of the acid in anhydrous alcohol. Recrystallization from alcohol gave colorless prisms, m.p. 186.5-188°. A sample mixed with β-dimethylaminopropionic acid hydrochloride melted at 186.5-188°.

SUMMARY

The decomposition products of taspine were investigated, and the supposition is put forward that the alkaloid is a diphenyl derivative and contains a $CH_2CH_2N(CH_3)_2$ side chain.

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SYNTHESIS OF ALIPHATIC ELEMENTOORGANIC COMPOUNDS BY THE DIAZO METHOD

VII. SYNTHESIS OF COMPOUNDS OF GROUP V ELEMENTS - ORGANOPHOSPHORUS COMPOUNDS. TRICHLOROMETHYLCHLOROPHOSPHINIC ACID AND ITS TRANSFORMATIONS

A. Ya. Yakubovich and V. A. Ginsburg

Since phosphorus trichloromethyltetrachloride has become an easily available substance due to the diazo method for the synthesis of chloromethyldichlorophosphine [1], it appeared desirable to attempt the preparation of trichloromethylphosphinic acid not from its esters, as was described earlier by the present authors [2], but by direct hydrolysis of CCl_3PCl_4. As was already noted [2] the hydrolysis of this tetrachloride in cold water is slow and incomplete, and therefore subsequently the hydrolysis was effected with water heated to 60-70°. In these conditions CCl_3PCl_4 is hydrolyzed rapidly with considerable evolution of heat. When the solution was evaporated in a vacuum at temperatures not above 40-50° and the substance then dried thoroughly in a desiccator over P_2O_5, a crystalline product was obtained, but its properties differed sharply from those of trichloromethylphosphinic acid formed by saponification of its esters. The substance described, which was 10 times as soluble in carbon tetrachloride and benzene and which deliquesced in the presence of moisture, had m.p. 79°, and considerable depression of melting point was observed when a sample was mixed with known trichloromethylphosphinic acid (m.p. 87°). Titration of aqueous solutions of this substance showed that is is not a di-, but a monobasic acid. This same acid is formed by the hydrolysis of the dichloroanhydride of trichloromethylphosphinic acid in analogous conditions.

Analytical data showed that this acid (with m.p. 79°) contained four chlorine atoms in the molecule, and corresponded to the empirical formula $CCl_3PO(Cl)OH$. However, the unusual nature of such a molecule, with a hydroxyl group together with an acid chloride atom at the phosphorus atom, and also the unusual stability of the "acid halide" chlorine to hydrolysis, led us to undertake further researches in order to confirm the proposed structure of this compound. The following was established: water and 0.5 N aqueous solution of caustic potash in the cold do not split off halogen from this acid; when a sample of the substance is boiled a long time (4 hours) with 0.5 N aqueous caustic potash solution, all 4 halogen atoms are split off. In analogous conditions trichloromethylphosphinic acid also decomposes completely. When an aqueous solution of the acid with m.p. 79° is heated with silver nitrate solution, a precipitate is formed. When concentrated aqueous solutions of these reagents are used in the cold, the precipitate forms slowly (after several days), and the precipitate consists of AgCl and the disilver salt of trichloromethylphosphinic acid, $CCl_3PO(OAg)_2$, which are formed in equimolecular proportions. If the acid with m.p. 79° is heated in an ampoule with hydrochloric acid in conditions for the saponification of trichloromethylphosphinic acid esters, trichloromethylphosphinic acid with m.p. 87° is formed. When a mixture of the acid with m.p. 79° and excess aniline in benzene is allowed to stand a long time at room temperature, no anilide formation or hydrogen chloride evolution occurs.

When this reaction is carried out in solution, dilution with a large amount of benzene results in the quantitative precipitation of an aniline salt of the acid with m.p. 79°, which differs from the aniline salts of trichloromethylphosphinic acid both by its melting point and by its titration behavior with methyl orange and phenolphthalein (monobasic), and by its much higher solubility in organic solvents (alcohol, aniline, acetone). The analytical data for this salt agreed with the calculated values for the compound $CCl_3PO(Cl)OH \cdot C_6H_5NH_2$.

When the acid with m.p. 79° is treated with excess (3 moles: 1 mole) of a moist solution of diazoethane or diazomethane in ether, acid esters of the type $CCl_3PO(OR)OH$ are formed, which have the properties of monobasic acids and which yield aniline salts of the type $CCl_3PO(OR)OH \cdot C_6H_5NH_2$, which are identical with the salts obtained by the treatment of the dimethyl and diethyl esters of trichloromethylphosphinic acid with aniline [2]. Vacuum distillation of the acid ethyl ester formed is accompanied by decomposition, and the distillation products are found to contain the fully substituted ethyl ester of trichloromethylphosphinic acid, formed in low yield. A second treatment of the acid ethyl ester with diazoethane leads to the formation of the complete ester in a yield of 50-70% on the original acid ester.

Since, as we have repeatedly observed, moist solutions of aliphatic diazo compounds are active hydrolytic agents, the course of the above reactions is explained as follows:

$$CCl_3PO(Cl)OH + CH_3CHN_2 \longrightarrow CCl_3PO(Cl)OC_2H_5 + N_2$$

$$CCl_3PO(Cl)OC_2H_5 + H_2O + CH_3CHN_2 \longrightarrow CCl_3PO(OC_2H_5)OH + N_2 + CH_3CH_2Cl$$

$$CCl_3PO(OC_2H_5)OH + CH_3CHN_2 \longrightarrow CCl_3PO(OC_2H_5)_2 + N_2.$$

Here the removal of hydrogen chloride from the reaction zone apparently favors the relatively rapid hydrolysis of the intermediately formed chloro ester.

For a final determination of the structure of the acid ester of trichloromethylphosphinic acid it was desirable to obtain it from a definitely known compound – the diethyl ester of trichloromethylphosphinic acid – and to compare the two products. With this aim in view, the fully substituted ethyl ester of trichloromethylphosphinic acid was saponified in mild conditions – by aqueous caustic baryta solution at 50-60° – and also slowly saponified with the aid of hydrochloric acid at room temperature.

The first method did not give the desired results, as it was found that at 50-60° the original ester is quantitatively decomposed by baryta solution to form chloroform and phosphoric acid

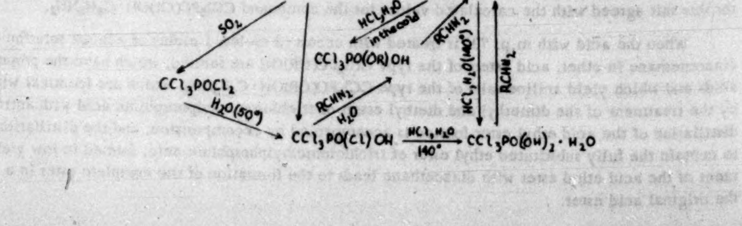
$$CCl_3PO(OC_2H_5)_2 + 3H_2O \xrightarrow{Ba(OH)_2} CHCl_3 + H_3PO_4 + 2C_2H_5OH.$$

The second method, when the diethyl ester was saponified by hydrochloric acid at room temperature over a period of three months, gave the expected acid ester $CCl_3PO(OC_2H_5)OH$ which, with aniline, formed a salt identical with the aniline salt obtained by the diazoethane treatment of the acid with m.p. 79°, as described above.

In order to establish whether the acid with m.p. 79° has a structure similar to that of trichloromethylphosphinic acid, and only differs from it in having a difficultly hydrolyzed chlorine atom instead of a hydroxyl group at the phosphorus atom, it was of interest to attempt to convert the acid with m.p. 87°, or its derivatives, into the acid with m.p. 79°. Treatment of $CCl_3PO(OH)_2$ with phosphorus pentachloride or thionyl chloride did not answer the problem. This gave organophosphorus compounds of a polymeric type, which upon treatment with water were converted into an unknown organophosphorus acid with m.p. 109-110°, which was not studied further. However, the reaction of the diethyl ester of trichloromethylphosphinic acid with phosphorus pentachloride yielded an acid chloride which after hydrolysis formed an acid with m.p. 79°, identical with the acid formed by the hydrolysis of phosphorus trichloromethyltetrachloride. It must be pointed out that this reaction between the ester of trichloromethylphosphinic acid and PCl_5 does not take place in the cold, but occurs only at 150°.

A final confirmation of the structure of the acid with m.p. 79° was provided by the results of optical analysis of trichloromethylphosphinic compounds. Infrared spectrum study of the acid with m.p. 79° showed the presence of the following bonds in the molecule: a) $P=O$ (1261 cm^{-1}); b) $C-Cl$ (1529 cm^{-1}); c) $O-H$ (3400 cm^{-1}); d) $P-Cl$ (combinational scattering spectrum, 487 cm^{-1}). These results fully confirm the validity of the proposed structure for the acid with m.p. 79°, as $CCl_3PO(Cl)OH$.

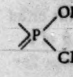
By the above study of the chemical properties of the trichloromethylphosphine derivatives obtained from chloromethyldichlorophosphine and from the esters of trichloromethylphosphinic acid it was possible to establish the relationship between them which may be expressed by the following scheme:



Study of the chemistry of trichloromethyl phosphorus compounds led to the general conclusion that the introduction of three chlorine atoms at the carbon atom of methylphosphine derivatives results in a number of peculiarities in their chemical behavior, of which the most important are the following: a) a sharp decrease in the activity of the P–Cl bond to hydrolysis and ammonolysis (with aniline); b) weakening of the C–P bond to the action of alkalies, when the $CCl_3{-}P$ group behaves like $CCl_3{-}C$ and $CCl_3{-}Si$, which in many instances are easily split by the action of alkalies:

$$CCl_3{-}P \xrightarrow{HOH} CCl_3H + HOP\equiv$$
$$CCl_3{-}C \xrightarrow{HOH} CCl_3H + HOC\equiv$$
$$CCl_3{-}Si \xrightarrow{HOH} CCl_3H + HOSi\equiv;$$

c) there is also a resemblance between trichloromethylphosphine compounds and substances of the chloral type in the tendency of trichloromethylphosphinic acid to form stable hydrates [2]; d) the introduction of a halogen atom into the methyl group of methylphosphinic acid leads to an increase in the acidity of these substances, so that chlorobromomethylphosphinic and trichloromethylphosphinic acids acquire the power of forming dianiline salts; e) the presence of a CCl_3 group attached to the phosphorus leads to the possibility of an unusual molecule of a semi acid-chloride type, which has both a halogen atom and a hydroxyl group simultaneously linked to the phosphorus atom,



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We must note a certain resemblance between the behavior of the acid chlorides of trichloromethylphosphinic acid and compounds of the "Boyd's chloroanhydride" type which are acid dichlorides of triarylmethylphosphinic acids. These latter are so resistant to hydrolysis that the acid chloride atoms are not hydrolyzed even after many hours of boiling with alkali. The second chlorine atom, linked to phosphorus is particularly inert in "Boyd's chloroanhydride"; this, as was shown by A. E. Arbuzov and B. A. Arbuzov [3] does not react even with such substances as alkali metal alcoholates. It is seen that the presence of three negative chlorine atoms linked to carbon in a methyl group confers properties on the molecule of the acid chloride of methylphosphinic acid which are similar to the properties produced by the introduction of three aryl radicals into the methyl group.

EXPERIMENTAL

Hydrolysis of phosphorus trichloromethyltetrachloride. Preparation of trichloromethylchlorophosphinic acid – $CCl_3PO(Cl)OH$. Phosphorus trichloromethyltetrachloride, prepared by the chlorination of 20 g of chloromethyldichlorophosphine, was gradually added to 30 ml of water with stirring. The reaction was sluggish at first, but as the water became warm the subsequent hydrolysis terminated very rapidly and the tetrachloride dissolved completely. The water was removed from the aqueous solution under vacuum at a temperature not higher than 30-40°, the crystals formed were pressed out on a porous plate, and the remaining moisture was removed in a vacuum desiccator over P_2O_5.

The yield was 27 g of colorless needle shaped crystals which melted at 79° after recrystallization from benzene (solubility 10 g in 200 ml of benzene at 70°). The substance is easily soluble in hot CCl_4 (17 g in 200 ml), badly in cold, and deliquesces in water, alcohol, and acetone.

3.915 mg sub.: 0.789 mg CO_2; 0.602 mg H_2O. 3.890 mg sub.: 0.758 mg CO_2; 0.534 mg H_2O. 0.0344 g sub. (sealed tube): 5.87 ml 0.1 N $AgNO_3$. 0.030 g sub. (sealed tube): 5.51 ml 0.1 N $AgNO_3$. 0.0486 g sub.: 0.4004 g molybdate. 0.1052 g sub.: 0.8799 g molybdate. 0.1698 g sub.: 7.30 ml 0.1 N KOH (methyl orange); 7.83 ml (phenylphthalein). 0.1562 g sub.: 6.65 ml 0.1 N KOH (methyl orange); 7.05 ml (phenylphthalein). Found %: C 5.49, 5.39; H 1.72, 1.53; Cl total 64.85, 65.11; P 13.62, 13.78. Equiv. (methyl orange) 230, 232, (phenylphthalein) 214, 218. $CCl_3PO(Cl)OH$. Calculated %: C 5.50; H 0.46; Cl total 65.14; P 14.22. Equiv. 218.

Determination of the molecular weight in acetophenone gave a high value (270). The substance forms no insoluble Ag salts in the cold; prolonged heating of the acid $CCl_3PO(Cl)OH$ and $AgNO_3$ leads to the formation of a precipitate consisting of $CCl_3PO(OAg)_2$ and AgCl, formed in equimolecular proportions.

Hydrolysis of the acid dichloride of trichloromethylphosphinic acid. 20 g of CCl_3POCl_2 was hydrolyzed by 30 ml of water warmed to 50°, and excess water was then removed under vacuum. Careful drying yielded 17 g of needle-like crystals, m.p. 79°; the substance was identical with the acid obtained by the hydrolysis of phosphorus trichloromethyltetrachloride.

Preparation of the aniline salt of trichloromethylchlorophosphinic acid $CCl_3PO(Cl)OH \cdot C_6H_5NH_2$. 3 g of aniline was added to a solution of 2 g of $CCl_3PO(Cl)OH$ in 260 ml of benzene and the mixture left for twenty-four hours. The precipitate was then filtered off and washed with benzene. Fine needles, m.p. 190-191° (decomp.).

4.500 mg sub.: 4.530 mg CO_2; 1.380 mg H_2O. 5.150 mg sub.: 5.163 mg CO_2; 1.565 mg H_2O. 5.805 mg sub.: 0.2450 ml N_2 (26°, 743 mm). 5.500 mg sub.: 0.2254 ml N_2 (26°, 743 mm). 9.450 mg sub.: 2.420 ml 0.05 N $AgNO_3$. 0.1202 g sub.: 3.90 ml 0.1 N KOH (phenolphthalein). 0.1250 g sub.: 4.00 ml 0.1 N KOH. Found %: C 27.45, 27.43; H 3.43, 3.41; N 4.77, 4.65; Cl 45.45. Equiv. 307. $CCl_3PO(Cl)OH \cdot C_6H_5NH_2$. Calculated %: C 27.10; H 2.65; N 4.51; Cl 45.80. Equiv. 312.

Hydrolysis of trichloromethylchlorophosphinic acid. Conversion of the acid with m.p. 79° into trichloromethylphosphinic acid. 1 g of the acid $CCl_3PO(Cl)OH$ with m.p. 79° was heated for 3 hours at 140° with 5 ml of 15% hydrochloric acid. After removal of water under vacuum the crystalline mass was dried over P_2O_5 and recrystallized from benzene. Needles, m.p. 87°. The substance forms an insoluble silver salt which explodes on heating. A sample mixed with known trichloromethylphosphinic acid gave no melting point depression.

Reaction of trichloromethylchlorophosphinic acid with diazoethane. a) Preparation of the acid ethyl ester of trichloromethylphosphinic acid $CCl_3PO(OC_2H_5)OH$. A solution of 5.5-6 g (3 moles) of diazoethane in 300 ml of ether (the ether solution of diazoethane was not dried in this instance) was added dropwise to 6 g (1 mole) of the acid $CCl_3PO(Cl)OH$ with m.p. 79° in 50 ml of ether at −10°. The decomposition of the diazo compound was vigorous at first and then slowed down. After the diazo compound disappeared from the solution the ether solution was dried over sodium sulfate and the ether distilled off with the aid of a fractionating column. The residue was 7.2 g of a thick faintly colored liquid which slowly dissolved in water to give an aqueous solution with an acid reaction. The product was the impure acid ethyl ester of trichloromethylphosphinic acid.

0.0538 g sub.: 15.45 ml 0.1 N $Na_2S_2O_3$. 0.0715 g sub.: 20.06 ml 0.1 N $Na_2S_2O_3$. Found %: OC_2H_5 21.56, 21.06. $CCl_3PO(OC_2H_5)OH$. Calculated %: OC_2H_5 19.85.

When distilled in vacuum the acid ester decomposed with the formation of a small amount of the diethyl ester of trichloromethylphosphinic acid with b.p. 122-123° at 12 mm, d_0^{14} 1.3670, n_D^{20} 1.4610 and of other lower-boiling products.

b) Preparation of the aniline salt of the acid ethyl ester of trichloromethylphosphinic acid. 2 g of aniline was added to a mixture of 1 g of the acid ester (see the previous experiment) and 25 ml of benzene. Fine small needles of the salt were immediately precipitated. After 4 hours the precipitate was separated off and washed with benzene. M.p. 175-176° (decomp.); a sample mixed with the substance obtained by another method previously [2] gave no melting point depression.

0.0512 g sub.: 9.34 ml 0.1 N $Na_2S_2O_3$. 0.0183 g sub.: 3.57 ml 0.1 N $Na_2S_2O_3$. 0.1027 g sub.: 3.24 ml 0.1 N KOH. 0.1488 g sub.: 4.73 ml 0.1 N KOH (phenolphthalein). Found %: OC_2H_5 13.54, 14.66. Equiv. 317, 315. $CCl_3PO(OC_2H_5)OH \cdot C_6H_5NH_2$. Calculated %: OC_2H_5 14.04. Equiv. 320.5.

c) Reaction of the acid ethyl ester of trichloromethylphosphinic acid with diazoethane. A solution of 2.7 g (3 moles) of diazoethane in 120 ml of ether was added to a solution of 4 g (1 mole) of the acid ethyl ester of trichloromethylphosphinic acid (prepared as described in Experiment "a") in 50 ml of ether at −5°. After the excess diazoethane decomposed overnight and the solution became colorless, it was dried with sodium sulfate and the ether was distilled off. The residue (4.5 g) was fractionated. Most of the liquid distilled at 115-130° (13 mm). A second fractionation yielded the diethyl ester of trichloromethylphosphinic acid with b.p. 122° (12 mm), d_0^{14} 1.3690, n_D^{20} 1.4620.

0.0702 g sub.: 32.81 ml 0.1 N $Na_2S_2O_3$. 0.0862 g sub.: 40.88 ml 0.1 N $Na_2S_2O_3$. Found %: OC_2H_5 34.87, 35.32. $CCl_3PO(OC_2H_5)_2$. Calculated %: OC_2H_5 35.22.

Preparation of trichloromethylchlorophosphinic acid from the diethyl ester of trichloromethylphosphinic acid by the action of phosphorus pentachloride. a) Preparation of trichloromethylchlorophosphinic acid. 15 g of PCl_5 was added to 4 g of the diethyl ester of trichloromethylphosphinic acid and the mixture heated for 1 hour at 150°. 5 g of $POCl_3$ was driven off in the process. The residue solidified on cooling; treatment with sulfur dioxide converted it into a liquid. After removal (under vacuum) of the last remains of phosphorus oxychloride a viscous mass remained, which was extracted with 10 ml of hot water and the water removed under vacuum, when 2.5 g of needle-shaped crystals remained in the flask. M.p. 78-79° after recrystallization from benzene. No melting point depression was found when a sample of the crystals was mixed with known trichloromethylphosphinic acid.

b) Reaction of trichloromethylphosphinic acid with PCl_5 and $SOCl_2$. The reactions between trichloromethylphosphinic acid and PCl_5 or $SOCl_2$ do not lead to the formation of the acid dichloride of trichloromethylphosphinic acid. After removal of $POCl_3$ or excess $SOCl_2$ under vacuum the residue was a solid mass of organophosphorus compounds insoluble in organic solvents. Treatment of this mass with water yields, after removal of the water under vacuum, a monobasic acid, m.p. 109-110°, with an equivalent weight of 190-200; this compound was not studied further.

Saponification of the diethyl ester of trichloromethylphosphinic acid by caustic baryta. 4.5 g of $CCl_3PO(OC_2H_5)_2$ was added dropwise at 60-80° to a suspension of 3 g of caustic baryta in 25 ml of water. There was an immediate reaction, chloroform being given off and collected in a receiver. The total yield was 2.2 g of chloroform, b.p. 61-62°, which gave the characteristic "isonitrile" reaction. Phosphate ions (by the reaction with ammonium molybdate) were detected qualitatively in the aqueous solution.

Saponification of the diethyl ester of trichloromethylphosphinic acid by hydrochloric acid in mild conditions. 4 g of $CCl_3PO(OC_2H_5)_2$ and 15% of hydrochloric acid were sealed in an ampoule and left at room temperature for 3 months. At the end of that time the reaction mixture was still separated into two layers. The ampoule was opened, the lower layer was combined with the residue obtained when water was removed under vacuum from the upper layer, the whole was dissolved in alcohol, and 2 g of aniline was added to the solution. 2.5 g of a precipitate was formed which, upon recrystallization from water formed needle-shaped crystals with m.p. 176° (decomp.). A sample mixed with the product obtained in the previous experiment showed no depression of melting point.

3.813 mg sub.: 4.675 mg CO_2; 1.462 mg H_2O. 13.605 mg sub.: 2.600 ml 0.05 N $AgNO_3$. 6.025 mg sub.: 0.2580 ml N_2 (23°, 746 mm). Found %: C 33.34; H 4.30; Cl 34.06; N 4.85. $CCl_3PO(OC_2H_5)OH \cdot C_6H_5NH_2$. Calculated %: C 33.67; H 4.05; Cl 33.23; N 4.37.

SUMMARY

1. Trichloromethylchlorophosphinic acid was prepared by the hydrolysis of phosphorus trichloromethyltetrachloride and phosphorus trichloromethyl oxychloride. Its properties and some peculiarities of its transformations have been studied. The relationships and conversions in the series of phosphorus trichloromethyl derivatives have been determined.

2. It is shown that the introduction of three chlorine atoms at the carbon atom of methylphosphine derivatives confers on the latter a number of peculiarities of chemical behavior. For example, the sensitivity of the P—Cl bond to hydrolysis and ammonolysis is reduced, the C—P bond is weakened toward the action of alkalies capable of splitting it with the formation of chloroform, and the phosphorus atom acquires the power of simultaneously retaining a halogen atom and a hydroxyl group.

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* T. p. = C. B. Translation pagination.

ADDITION OF NITROSYL CHLORIDE TO FLUORINATED OLEFINS.II

A. Ya. Yakubovich, V. A. Shpansky, and A. L. Lemke

In an earlier paper [1] the results of a study of the addition of nitrosyl chloride to chlorinated olefins were described; it was then established that in most instances the addition of nitrosyl chloride takes place in accordance with the polarity of the reacting bonds, so that the positive NO group is directed toward the negatively charged carbon atom joined to a double bond, while the negative halogen is directed toward the positively charged carbon atom.

It was of interest to determine the extent to which this orientation holds in the reactions between nitrosyl chloride and fluorinated ethylene derivatives.

The reaction of nitrosyl chloride with vinyl fluoride, 1,2-fluorochloroethylene, 1-fluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, and trifluorochloroethylene was studied.

The addition of nitrosyl chloride to vinyl fluoride (and the other reactions) was brought about by the usual method – in ampoules at room temperature. The molar ratio of the reagents was 1 : 1. Fractionation of the reaction mixture yielded, in addition to a substance without nitrogen (1,2-dichloro-1-fluoroethane), a compound with b.p. 55.5° at 8 mm as the main reaction product. Analysis, molecular weight, and properties of this substance showed that it is a nitro-compound with the composition $C_2H_3ClFNO_2$ (yield 54%).

By analogy with the reaction with vinyl chloride, which proceeds normally, in the case of vinyl chloride the reaction should follow the scheme:

$$\overset{(\delta+)}{\text{FCH}}=\overset{(\delta-)}{\text{CH}_2}+\overset{(\delta-)(\delta+)}{\text{ClNO}}\longrightarrow \text{FClCHCH}_2\text{NO}\xrightarrow{\text{ClNO}}\text{FClCHCH}_2\text{NO}_2.$$

In fact, the nitrofluorochlorethane formed, as was shown by its positive nitrol reaction, proved to be 1-nitro-2,2-fluorochloroethane.

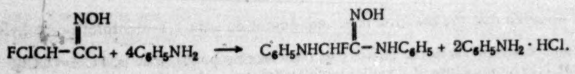
Nitrosyl chloride also reacted just as readily with 1,2-fluorochloroethylene; here the expected reaction should follow the scheme: *

$$\overset{(+)}{\text{FCH}}=\overset{(-)}{\text{CHCl}}+\overset{(\delta-)(\delta+)}{\text{ClNO}}\longrightarrow \text{FClCHCHClNO}.$$

This, in fact, occurs. The main product of the reaction between fluorochloroethylene and nitrosyl chloride is the acid chloride of fluorochloroacetohydroxamic acid, obtained in approximately 45% yield:

$$\text{FClCH}-\text{CHClNO}\longrightarrow \text{FClCHCCl}=\text{NOH}.$$

One proof, among others, of the structure of the compound as the acid chloride of a hydroxamic acid is its reaction with aniline, which occurs very readily with the formation of phenylaminofluoroacetohydroxamic acid anilide:



$$\text{FClCH}-\overset{\overset{\text{NOH}}{\|}}{\text{C}}\text{Cl}+4\text{C}_6\text{H}_5\text{NH}_2\longrightarrow \text{C}_6\text{H}_5\text{NHCHF}\overset{\overset{\text{NOH}}{\|}}{\text{C}}-\text{NHC}_6\text{H}_5+2\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}.$$

It is interesting to note that in reactions between nitrosyl chloride and halogenated ethylene derivatives which give rise to primary nitroso compounds (condensation with vinyl chloride, allyl chloride, etc.) the latter are oxidized

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* Here and subsequently the signs (+) and (–) indicate only the relative electron density distributed in the C–C bond, that is, the direction of the dipole in this bond.

to nitro compounds. If, however, halogen is present at the carbon which becomes linked to the nitroso group (condensation with 1,2-fluorochloroethylene), a nitroso-oxime regrouping takes place with the formation of a hydroxamic acid halide. This is apparently to be explained by the specific influence of the α-chlorine atom, which has a greater inhibiting effect on oxidation than on the regrouping.

It is more difficult to determine the polarity of the C−C bond in the case of trihalogen substituted ethylene derivatives, when the halogen atoms are different, as for example, in 1,1-difluoro-2-chloroethylene or 1,1-dichloro-2-fluoroethylene.

Nevertheless, it may be assumed for difluorochloroethylene that the carbon atom charges are distributed as shown below. Consequently, the condensation of 1,1-difluoro-2-chloroethylene with nitrosyl chloride should be expected to follow the scheme:

$$\overset{(+)}{F_2C}=\overset{(-)}{CHCl}+\overset{(\delta-)(\delta+)}{ClNO}\longrightarrow F_2ClCCHClNO.$$

A study of this reaction showed that it takes a more complex course, and the main reaction product is a high molecular polymeric compound. When this polymer was heated in a vacuum it depolymerized and formed a substance with the composition $C_6HO_2N_2Cl_5F_4$, the structure of which was not studied further. In addition to the polymer, 1,1-dichloro-2,2,2-difluoronitroethane was formed in very low yield.

Apparently the polymer is formed as the result of changes in the normal addition product of nitrosyl chloride and difluorochloroethylene. These changes may be represented by the following series of equations:

$$F_2ClCCHClNO\xrightarrow{-HF}FClC=CClNO$$

$$2CFCl=CClNO+CF_2=CHCl\longrightarrow(C_6HN_2O_2F_4Cl_5)_n.$$

This assumption is based both on the result of the previously studied analogous addition reaction between nitrosyl chloride and vinylidene chloride, leading to the formation of 1,1-dichloro-2-nitroethylene

$$Cl_2C=CH_2\xrightarrow{ClNO}Cl_3CCH_2NO\longrightarrow Cl_3CCH_2NO_2\xrightarrow{-HCl}Cl_2C=CHNO_2,$$

and on data for the composition of the depolymerization product formed when the polymer is heated in a vacuum.

The normal course for the addition of nitrosyl chloride, put forward above, is also confirmed by the fact that the 1,1-dichloro-2,2,2-difluoroethane formed in the reaction is a stable compound and is obtained in very low yield, which indicates that the addition reaction between nitrosyl chloride and difluorochloroethane in a direction opposite to that dictated by the polarity of the reacting bonds is not the principal direction for the reaction between these substances.

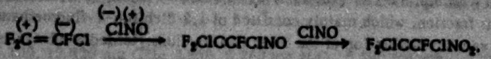
The reaction between nitrosyl chloride and 1,1-dichloro-2-fluoroethylene in conditions analogous to those for the reaction with difluorochloroethylene takes place with the formation of 1,1-fluorochloro-2,2,2-dichloronitroethane in 55% yield and of a certain amount of a tertiary nitroso compound, apparently 1,1-fluorochloro-2,2,2-dichloronitrosoethane. This last compound could not be isolated in the pure state because the reaction mixture contained a nitrogen-free substance with a boiling point close to the boiling point of the nitroso compound formed. Thus, the main direction of the reaction between nitrosyl chloride and dichlorofluoroethylene follows the scheme:

$$FCH=CCl_2+ClNO\longrightarrow FClCHCCl_2NO\xrightarrow{ClNO}FClCHCCl_2NO_2.$$

It may be assumed that the reaction under consideration with 1,1-dichlorofluoroethylene proceeds normally in a direction which corresponds to the polarity of the reacting bonds, that is, $\overset{(+)}{FCH}=\overset{(-)}{CCl_2}$, as should follow if only from the fact that 1,1-fluorochloro-2,2,2-dichloronitroethane is the only condensation product formed in the process in a good yield.

Of the per-halogenated ethylene derivatives, the condensation of trifluorochloroethylene was studied, the carbon atoms of which are polarized as follows: $\overset{(+)}{F_2C}=\overset{(-)}{CFCl}$.

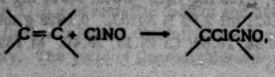
The addition of nitrosyl chloride to trifluorochloroethylene proceeds rather more slowly than in the other instances considered above; in addition to a nitroso compound and the chlorination product of trifluorochloroethylene, the main reaction product here is trifluorodichloronitroethane. From the polarity of the ethylene bond in trifluorochloroethylene it may be assumed that the direction of the addition reaction and the structure of the nitro compound formed are given by the scheme:

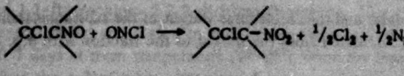


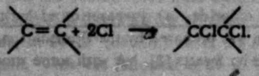
$$\overset{(+)}{F_2C}=\overset{(-)}{CFCl}\xrightarrow{\overset{(-)(+)}{ClNO}}F_2ClCCFClNO\xrightarrow{ClNO}F_2ClCCFClNO_2.$$

Thus, from the results of our study of addition reactions between nitrosyl chloride and halogenated ethylene derivatives it may be concluded that in most instances nitrosyl chloride is added on to the ethylene bond in the manner dictated by the polarities of the reacting bonds.

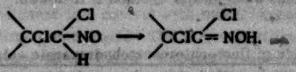
The general scheme of the addition reactions may be expressed as follows:

1. 

2. 

3. 

If an α-halogenated nitroso compound is formed as the result of nitrosyl chloride addition, the oxidation reaction is inhibited, and in the presence of a hydrogen atom a nitroso-oxime regrouping takes place:



With α-dihalogen nitroso compounds oxidation is also inhibited, and in addition to the nitro product the formation of intermediate nitroso compounds may be detected.

EXPERIMENTAL

The Experimental Section, in addition to a description of the addition reaction of nitrosyl chloride, contains details of the preparation of the original fluorochloroderivatives of ethane and ethylene. Most of these compounds have been described previously by others, who prepared them by various methods. Here we give only descriptions of syntheses in which the methods described in the literature were modified in some way. The constants of the fluorides obtained in most instances coincided with those cited in the literature. An exception was 1,1-difluoro-2-dichloroethylene, the boiling point of which, according to Henne and Ladd [2] is −2.4°, while in reality this substance boils at −15.5°.

1. Reaction of vinyl fluoride with nitrosyl chloride. a) Preparation of vinyl fluoride. A solution of sodium butylate (or amylate) prepared from 550 g of butyl alcohol and 17 g of sodium was placed in a round bottomed flask fitted with a dropping funnel and a reflux condenser. The condenser was connected to a trap immersed in freezing mixture (acetone + carbon dioxide). The sodium butylate solution was heated to a temperature close to 100°, and 74 g of chlorofluoroethane was added from the dropping funnel dropwise during 3-4 hours. The reaction products condensed in the cooled trap. During the reaction the temperature was so maintained that the liquid boiled gently; at the end of the addition of chlorofluoroethane the mixture was heated another 40-50 minutes. The condensate in the trap, which consisted mainly of vinyl chloride, was distilled with the aid of a fractionating column. After a 2-fold distillation vinyl fluoride was obtained, boiling at −71°, −67°. The yield was 1 g, which was about 10%. The boiling point of the pure vinyl fluoride, isolated by repeated distillation, was −71, −72°.

b) Preparation of 1,1-fluorochloro-2-nitroethane. A total amount of 10 g of vinyl fluoride and 16.5 g of nitrosyl chloride was placed in four thick-walled tubes cooled by a mixture of acetone and carbon dioxide. The tubes were sealed and left for 3 days at room temperature. The reaction mass acquired a dark green color. The cooled tubes were opened (increased pressure) and after the usual treatment their contents were fractionated first under atmospheric pressure and then under vacuum. The following fractions were obtained: 1st, 77-113° (760 mm), 9.1 g; 2nd, 114-128° (760 mm), 8.9 g; and 3rd, 48-66° (15 mm), 5.1 g.

The fraction with b.p. 77-113° (760 mm) was a colorless liquid with the characteristic odor of chlorinated hydrocarbons. This fraction, which mainly consisted of 1,2-dichloro-1-fluoroethane (b.p. 73.7°) was not studied further. A second vacuum distillation of the other two fractions yielded a substance (8.7 g) which boiled at 50-65° (18 mm), the main bulk distilling at 54-57°.

Another distillation gave this substance in the pure state with b.p. 55.5° (18 mm). It was a colorless liquid, d_4^{20} 1.4961, n_D^{20} 1.4644 with a sharp odor. The substance is slightly soluble in water and is gradually hydrolyzed by water, chloride ions being found in the solution. It dissolves in 10% aqueous caustic soda giving an orange-yellow color, and gives a positive nitrol reaction for primary nitro groups.

6.679, 4.905 mg sub.: 4.769, 3.502 mg CO_2; 1.659, 1.109 mg H_2O. 4.315, 5.920 mg sub.: 0.407, 0.544 ml N_2 (23°, 24°, 746, 744 mm).12.525, 6.080 mg sub.: 5.14, 2.521 ml 0.02 N $AgNO_3$. 0.1328 g sub.: 13.48 g benzene: Δt 0.375°. Found %: C 19.46, 19.47; H 2.78 2.51; N 10.34, 10.68; Cl 29.15, 29.40. M 132.6. $C_2H_3O_2NClF$. Calculated %: 18.8; H 2.37; N 10.98; Cl 27.8. M 127.5.

The above properties, analytical data, and the molecular weight of the substance indicate that it is 1,1-chlorofluoro-2-nitroethane. The yield (calculated from the weight of the fraction with b.p. 50-65° at 18 mm) was 54% based on the nitrosyl chloride used.

2. Reaction of 1,2-fluorochloroethylene with nitrosyl chloride. a) Preparation of 1-fluoro-1,2,2-trichloroethane and 1-chloro-2-fluoroethylene. Fluorochloroethane was prepared by the fluorination of symmetrical tetrachloroethane by antimony fluoride, by the method described by Swarts [3], but with some modifications. The reaction was carried out not in a copper apparatus, but in glass, and the catalyst used was antimony pentachloride activated by the addition of a small amount of bromine. These minor deviations from Swarts' method had the effect that the fluorination resulted mainly in the formation of fluorotrichloroethane and not of difluorodichloroethane, which is obtained in considerable amounts when Swarts' method is followed. The fluorochloroethylene was prepared strictly by the method given by Swarts.

b) Preparation of the acid chloride of fluorochloroacetohydroxamic acid. 18.5 g of fluorochloroethylene and 13 g of nitrosyl chloride were placed in thick-walled glass tubes cooled by a mixture of acetone and carbon dioxide, and the tubes were then sealed. The mixture was held at room temperature (18-20°) during 72 hours, and the tubes were then cooled and opened. Increased pressure was noted during the opening. The color of the reaction mixture changed from dark red to brownish-red, and as the unreacted components evaporated from the opened tubes, to green. After removal of the unreacted components (8.5 g) the reaction mixture was subjected to vacuum distillation. When heated during the distillation in the distilling flask, the liquid became colorless. The distillate was divided into 3 fractions: 1st — 3.3 g of a colorless liquid boiling at 42-73° at 60 mm (this substance did not contain nitrogen and was not studied further); 2nd — 10 g of a colorless liquid, b.p. 75-85° at 60 mm; the 3rd fraction (3.4 g) distilled in the range 93-110°; the residue in the flask was 2.2 g. The 3rd fraction, as another distillation showed, mainly (2 g) consisted of the substance contained in the 2nd fraction.

Distillation of the fraction boiling at 75-85° at 60 mm yielded a colorless liquid with b.p. 76-78° at 60 mm, d_4^{20} 1.5749 and n_D^{20} 1.4472. The substance has a sharp odor, is soluble in water and the common organic solvents, and gives the hydroxamic reaction with ferric chloride. Aqueous solutions contain considerable amounts of chloride ions. The molecular weight, analytical data, and the properties of the substance indicate that it is the acid chloride of fluorochloroacetohydroxamic acid. The yield of the acid chloride with b.p. 75-85° at 60 mm was about 45% calculated on the reacted nitrosyl chloride.

8.759, 6.444 mg sub.: 5.320, 3.943 mg CO_2; 0.960, 0.720 mg H_2O. 5.795, 5.970 mg sub.: 0.451, 0.431 ml N_2 (22°, 752 mm). 6.615, 5.975 mg sub.: 4.281, 3.90 ml 0.02 N $AgNO_3$. 0.3000 g sub.: 0.0810 g CaF_2. 0.2235 g sub.; 30.00 g benzene: Δt 0.254°. Found %: C 16.58, 16.69; H 1.27, 1.25; N 8.89, 9.04; Cl 45.9, 46.24; F 13.14. M 146.7. $C_2H_2ONCl_2F$. Calculated %: C 16.44; H 1.37; N 9.6; Cl 48.7; F 13.01. M 146.

The substance, like most acid chlorides of hydroxamic acids, decomposes on keeping, forming a colorless crystalline precipitate and evolving hydrogen chloride. With aniline it gives the anilide of phenylaminofluoroacetohydroxamic acid.

To a solution of 1.6 g of the acid chloride of fluorochloroacetohydroxamic acid in 10 ml of anhydrous ether a solution of 3.1 g of aniline in 10 ml of anhydrous ether was added in portions. The reaction was accompanied by a small increase of temperature and the formation of a crystalline substance of a yellowish color. The anilide (1 g) with m.p. 156° was recrystallized from alcohol and dried in a vacuum desiccator.

It forms colorless shiny needles with m.p. 157°. The substance contains no chlorine and gives a positive reaction for fluorine.

6.255, 5.330 mg sub.: 15.100, 12.820 mg CO_2; 2.850, 2.280 mg H_2O. 5.593 mg sub.: 0.798 ml N_2 (24°, 760 mm). Found %: C 65.59, 65.81; H 4.79, 5.10; N 16.39. $C_{14}H_{14}ONF$. Calculated %: C 64.86; H 5.4; N 16.2.

3. Reaction of 1-fluoro-2,2-dichloroethylene with nitrosyl chloride. a) Preparation of fluorodichloroethylene. Fluorodichloroethylene was prepared by a method analogous to that described by Swarts [3].

70 g of fluorotrichloroethane was placed in an apparatus consisting of a round bottomed flask of 500 ml capacity fitted with a dropping funnel and connected to a fractionating column and a straight condenser. A solution of sodium amylate, prepared from 11.5 g of metallic sodium and 300 ml of isoamyl alcohol, was added by portions from the dropping funnel. The flask was heated carefully for several hours in such a way that the fluorodichloroethylene formed distilled off regularly. The yield of fluorodichloroethylene, with b.p. 37.5°, was 37 g.

b) Preparation of 1,1-fluorochloro-2,2,2-dichloronitroethane. 15 g of nitrosyl chloride (1.15 mole) and 22.5 g of dichlorofluoroethylene (1 mole) was sealed in each of two thick-walled tubes, with thorough cooling. The reaction mixture was left 7 days at room temperature (20-22°), when the liquid gradually darkened and finally attained a dark green color. When the cooled tubes were opened (increased pressure was noted), their contents were distilled under vacuum with the aid of a fractionating column. The unreacted components, about 35% of the original charge, distilled off first. Then, at 27-29° (50 mm) about 8 g of the nitroso compound formed in the reaction distilled in the form of a blue liquid. This was followed at 30-34° (50 mm) by several grams of a colorless liquid. Then an intermediate fraction (up to 64° at 33 mm) was obtained, and, at 64-70° (33 mm), about 25 g of fluorotrichloronitroethane in the form of a colorless liquid.

The nitroso compound was again distilled under vacuum with the aid of a fractionating column. It was observed that when the nitroso compound came into contact with rubber (stoppers and tubes) it immediately changed color, turning from a dark blue to a dirty-green liquid. The second distillation yielded 3 g of the nitroso compound in the form of a dark blue liquid with b.p. 28° at 8 mm. The nearly colorless residue from the distillation was fractionated together with the fraction boiling at 30-32° (30 mm); about 1 g of a colorless liquid with b.p. 30° (33 mm) or 53.5° (88 mm) was obtained. Elementary qualitative analysis of this substance showed that it contains chlorine but no nitrogen. This substance was not studied further. Analysis of the nitroso compound showed that it is not a single substance. It may be assumed that the nitroso compound was contaminated with a colorless nitrogen-free substance, which was probably fluorotetrachloroethane (b.p. 117° at 760 mm, according to Henne).

A second distillation of the fluorotrichloronitroethane fraction boiling at 64-70° (33 mm) gave pure fluorotrichloronitroethane (15 g). 1,1-Fluoro-2,2,2-dichloronitroethane boils at 68-69° (33 mm), d_4^{20} 1.677, n_D^{20} 1.399. The substance is insoluble in water and 10% caustic soda, does not decolorize aqueous permanganate solution, and does not liberate iodine from potassium iodide solution. It gives a characteristic reaction with dimethylaniline paper. The yield of fluorotrichloronitroethane boiling at 64-70° (33 mm) was 55% calculated on the reacted nitrosyl chloride.

6.979, 3.031 mg sub.: 3.343, 1.450 mg CO_2. 3.08, 3.815 mg sub.: 0.185, 0.226 ml N_2 (21°, 758 mm). 2.362, 3.541 mg sub.: 4.907, 7.358 mg AgCl. 0.1880 mg sub.: 9.0 ml 0.1 N $AgNO_3$. 0.1722 g sub.; 15.88 g benzene: Δt 0.295°. Found %: C 13.05, 13.06; N 6.86, 7.03; Cl 51.4, 51.41; F 9.04. M 189. $C_2HO_2NCl_3F$. Calculated %: C 12.28; N 7.16; Cl 54.4; F 9.72. M 195.5.

4. Reaction of 1,1-difluoro-2-chloroethylene with nitrosyl chloride. a) Preparation of 1,1-difluoro-1,2,2-trichloroethane. The preparation of difluorotrichloroethane with the aid of antimony trifluoride was described by Henne [2]. Below is given a description of the preparation of difluorotrichloroethane with the aid of hydrogen fluoride.

An autoclave made of special steel, of 2 liters capacity, was charged with 1000 g of pentachloroethane (prepared by the fractionation of the chlorination products of dichloroethane), 800 g of anhydrous 99% hydrogen fluoride, and 500 g of antimony pentachloride. The contents of the autoclave were heated gradually, during 5 hours, up to 165°; the pressure was maintained at 40-45 atm. The excess pressure was released through a copper tube, as described for trifluorotrichloroethane (see below). At 165° the pressure increase became very slow, and the contents of the autoclave were distilled off during 20 minutes into the same bath containing ice. The heavy liquid obtained was washed first with a weak solution of alkali, then with water, and dried with calcium chloride. Yield 670 g. The mixture of fluorides was distilled with the aid of a fractionating column; a small amount of a low-boiling fraction

(40-72°) was followed at 72-74° by almost pure trichlorodifluoroethane in a yield of 520 g, and then by a high-boiling fraction up to 115°.

b) Preparation of 1,1-difluoro-2-chloroethylene. 80 g of zinc dust and 300 ml of ethyl alcohol was placed in a flask fitted with a reflux condenser, the upper end of which was connected to a trap cooled to −60°. The contents of the flask were heated to boiling, and 150 g of difluorotrichloroethane was gradually added during 2 hours through a capillary funnel. A further 60 g of zinc dust was then added to the flask, and the contents heated for 2 hours. The gaseous products evolved condensed in the trap in the form of a colorless liquid. When the reaction products were distilled over a fractionating column, a small amount (about 5 g) of a low-boiling liquid distilled over (at minus 28-26°), then dichloroethylene in a yield of 40 g distilled at −15.5°. As the boiling point of the difluorochloroethylene obtained did not agree with that given by Henne and Ladd [2] (b.p. −2.4°), the substance was analyzed and its molecular weight determined.

7.91 ml sub.: 3.98 ml 0.02 N $AgNO_3$. 11.51 ml sub. weighs 51.01 mg (13°, 736 mm). Found %: Cl 36.0. M 107.5. C_2HClF_2. Calculated %: Cl 35.8. M 98.46.

c) Preparation of 1,1-dichloro-2,2,2-difluoronitroethane and of the polymeric reaction products. 30 g of difluorochloroethylene and the molar proportion of nitrosyl chloride were placed in thick-walled glass tubes cooled to −50°, and the tubes were then sealed. At first the tubes were left in the light (300 W lamp) at 0° for 12 hours. At the end of this time distillation of the contents of one of the tubes showed that the components did not react in these conditions. The tubes were then kept at room temperature (18-20°) and opened after 70 hours. The brownish-green liquid which was formed was fractionally distilled under vacuum. The reaction liquid was a mixture difficult to separate by fractionation. During the first distillation, in order to avoid losses of low-boiling substances and decomposition of the reaction mass, the pressure was so regulated that the temperature within the liquid did not exceed 45°. By repeated distillations it proved possible to isolate an individual substance with b.p. 52° at 150 mm (2 g).

Under atmospheric pressure this substance distils without decomposition at 99°, and is a colorless liquid (d_4^{20} 1.597, n_D^{24} 1.3982) with a sharp odor, insoluble in water and miscible with most organic solvents.

The substance gives no color with ferric chloride, does not liberate iodine from potassium iodide solution, does not reduce aqueous permanganate solutions, and does not form chlorine ions on shaking with water. It does not dissolve when shaken with 10% caustic soda solution. On pyrolysis it gives off oxides of nitrogen, which give a characteristic color with Griess reagent.

5.560, 4.702 mg sub.: 2.800, 2.335 mg CO_2; 0.630, 0.510 mg H_2O. 4.702, 4.130 mg sub.: 0.294, 0.255 ml N_2 (14°, 738 mm). 11.750, 12.793 mg sub.: 6.53, 7.24 ml 0.02 N $AgNO_3$. 0.1658, 0.1489 g sub.: 18.2, 17.08 ml 0.1 N $AgNO_3$. 0.1612 g sub.; 20.10 g benzene: Δt 0.231°. Found %: C 13.75, 13.54; H 1.27, 1.21; N 8.11, 8.16; Cl 40.07, 40.13; F 19.6, 21.8. M 177.6. $C_2HO_2NCl_2F_2$. Calculated %: C 13.33; H 0.56; N 7.78; Cl 39.4; F 21.11. M 179.9.

The properties, molecular weight, and elementary analysis of the substance indicate that it is 1,1-dichloro-2,2,2-difluoronitroethane.

After distillation of the low-boiling fraction, the distillation flask contained the main bulk of the reaction products in the form of a pale yellow thick and viscous mass. Vaccum distillation of this mass yielded a high-boiling fraction which was much less viscous than the original mixture, and which distilled in the range 110-180° at 18 mm. The residue solidified completely on cooling. During a second distillation at the same pressure the liquid distilled completely in the range 110-150°. During the third distillation it was distilled up to 136°, the main bulk distilling at 132° (18 mm).

This compound is a fairly thick colorless liquid (d_4^{20} 1.751) with a faint odor. It is insoluble in water and when shaken with the latter gives only a slight amount of ionic chlorine. When shaken with 35-50% alkali solution, the substance reacts with evolution of heat, and large amounts of ionic chlorine appear in the aqueous solution. It gives no color with ferric chloride and does not decolorize permanganate; even on heating the substance reacts only slowly with permanganate, and does not add on bromine. Oxides of nitrogen are formed on pyrolysis. Distillation of the substance with zinc dust gives a colorless liquid, neutral to litmus, with an odor resembling that of acetamide.

Elementary analysis on the molecular weight of this substance showed that its composition is close to the empirical formula $C_6HO_2N_2Cl_5F_4$. It was not studied further.

2.170, 3.415 mg sub.: 1.470, 2.29 mg CO_2; 0.408; 0.530 mg H_2O. 7.425, 4.870 mg sub.: 0.451, 0.304 ml N_2 (21° 742 mm). 0.1087 0.1094 g sub.: 14.12, 13.93 ml 0.1 N $AgNO_3$. 0.5435, 0.5472 g sub.: 0.2517, 0.2626 g

CaF_2.* 0.2815 g sub.; 20.69 g benzene: Δt 0.170°. Found %: C 18.46, 18.29; H 1.6, 1.29; N 6.78. 6.90; Cl 46.09, 45.1; F 22.55, 23.31. M 409.5. $C_6HO_2N_2Cl_5F_4$. Calculated %: C 18.65; H 0.26; N 7.25; Cl 45.93; F 19.69. M 386.3.

5. Reaction of trifluorochloroethylene with nitrosyl chloride. a) Preparation of 1,1,2-trifluoro-1,2,2-trichloroethane. 1 kg of technical hexachloroethane, 450 g of antimony pentachloride, and 850 g of anhydrous hydrogen fluoride were placed in an autoclave of special steel, of 2 liters capacity.

The contents of the autoclave were gradually heated during 5 hours to 160°; the pressure was maintained at 45-50°. Excess pressure was released through a copper tube joined to the valve of the autoclave and with its other end immersed in an iron bath containing crushed ice. At 160°, when the pressure began to increase only very slowly, the contents of the autoclave were distilled off through the same tube into the bath with ice. The heavy liquid formed was separated from water, washed with 2% caustic soda solution and then with water, and dried with calcium chloride. Yield 710 g. The product was distilled with the aid of a fractionating column; the first fraction collected (150 g), which distilled at 45-49°, was 1,1,2-trichloro-1,2,2-trifluoroethane (boiling point of the pure substance is 47.7°); this was followed by an intermediate fraction, most of which distilled at 72-75° (this was difluorotrichloroethane, formed by the fluorination of pentachloroethane contained in the original hexachloroethane). At 90-92° a fraction (85 g) which was symmetrical difluorotetrachloroethane (boiling point of the pure substance is 92.8°) was collected.

b) Preparation of trifluorochloroethylene. 80 g of zinc dust and 30 ml of ethyl alcohol were placed in a flask fitted with a reflux condenser the upper end of which was joined to a trap cooled to −60°. 150 g of trifluorochloroethane was gradually added during 3 hours into the flask from a dropping funnel, a further 40 g of zinc dust was then added, the mixture was heated and kept for another hour with gentle boiling. The gaseous trifluorochloroethylene formed was condensed in the trap. The yield of the condensate was 85 g. The product was distilled over a fractionating column, and 57 g of trifluorochloroethylene with b.p. −27.5° (boiling point of the pure substance is −27.9°) was obtained.

c) Preparation of 1,1,1-difluorochloro-2,2,2-fluorochloronitroethane. 57 g of trifluorochloroethylene (1 mole) and 39 g (1.2 mole) of nitrosyl chloride were poured into thick-walled glass tubes with cooling. The mixture was held at room temperature (18-20°) during 96 hours, and the tubes were then cooled to −70° and opened. Increased pressure in the tubes was noted. The color of the reaction mixture changed from dark red to pale brown. The tubes were left at room temperature, when the greater part of the unreacted components (35% of the charge) evaporated. The remaining liquid was washed twice with water and dried with calcium chloride. The yield of the reaction products was 62 g. The liquid was distilled under vacuum to separate it from tarry impurities, the vapor being cooled by a mixture of acetone and carbon dioxide. Most of the substance distilled below 40° (90 mm). The residue was 6 g. The distillate was again distilled with the aid of a fractionating column without use of vacuum; the liquid was separated into 3 fractions. The 1st fraction (8.2 g) distilled at 45-52°; 13 g of the liquid distilled at 52-72°, and 21.5 g at 73-80°. The residue after distillation was 5 g. Vacuum distillation of the residue yielded a mixture (2 g) which boiled in the range 41-100° at 17 mm, and from which the individual substances could not be separated. The 45-52° fraction was trifluorotrichloroethane contaminated with a nitroso compound. In a second distillation the main bulk of it distilled at 47-48° as a heavy liquid slightly colored pale blue by a trace of nitroso compounds (d_4^{20} 1.61, n_D^{25} 1.3598).

A second distillation of the fraction which boiled at 52-72° showed that it was a mixture consisting chiefly of trifluorotrichloroethane (the total yield of which was 60%) and a small amount (about 3 g) of a liquid with b.p. 76-78°, which was in the boiling range of the 3rd fraction.

The 3rd fraction with b.p. 73-80° after two distillations yielded a substance with b.p. 77-78°, which was pure trifluorodichloronitroethane.

Trifluorodichloronitroethane is a colorless liquid (d_4^{20} 1.6202, n_D^{20} 1.3727), insoluble in water and miscible with most organic solvents. The substance is insoluble in aqueous caustic soda, and forms nitrogen oxides on pyrolysis. The yield was 65% calculated on the reacted nitrosyl chloride.

13.480, 7.010 mg sub.: 6.058, 3.197 mg CO_2. 6.335, 5.977 mg sub.: 0.372, 0.352 ml N_2 (24°, 752 mm). 0.1241 g sub.: 12.64 ml 0.1 N $AgNO_3$. 0.6342 g sub.: 0.3533 g CaF_2. 0.1654 g sub.; 15.70 g benzene: Δt 0.280°. Found %: C 12.30, 12.45; N 6.68, 6.71; Cl 36.12; F 27.75. M 192.2. $C_2O_2NCl_2F_3$. Calculated %: C 12.12; N 7.07; Cl 35.82; F 28.79. M 198.

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* Fluorine was determined by Bokemüller's method.

SUMMARY

1. The reactions of nitrosyl chloride with vinyl fluoride, 1,2-fluorochloroethylene, 1-fluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, and trifluorochloroethylene have been studied.

2. The following were prepared and investigated: 1,1-fluorochloro-2-nitroethane, 1,1-fluorochloro-2,2,2-dichloronitroethane, 1,1-dichloro-2,2,2-difluoronitroethane, 1,1,1-difluorochloro-2,2,2-fluorochloronitroethane; the acid chloride of fluorochloroacetohydroxamic acid, and a substance with the composition $C_6HO_2N_2Cl_5F_4$, formed in the reaction between difluorochloroethylene and nitrosyl chloride.

3. The addition of nitrosyl chloride to the above fluorine derivatives of ethylene proceeds in accordance with the polarities of the reacting bonds, so that the positive nitroso group is directed to the negatively polarized carbon atom linked by an ethylene bond, while the negative chlorine is directed to the oppositely polarized carbon atom.

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